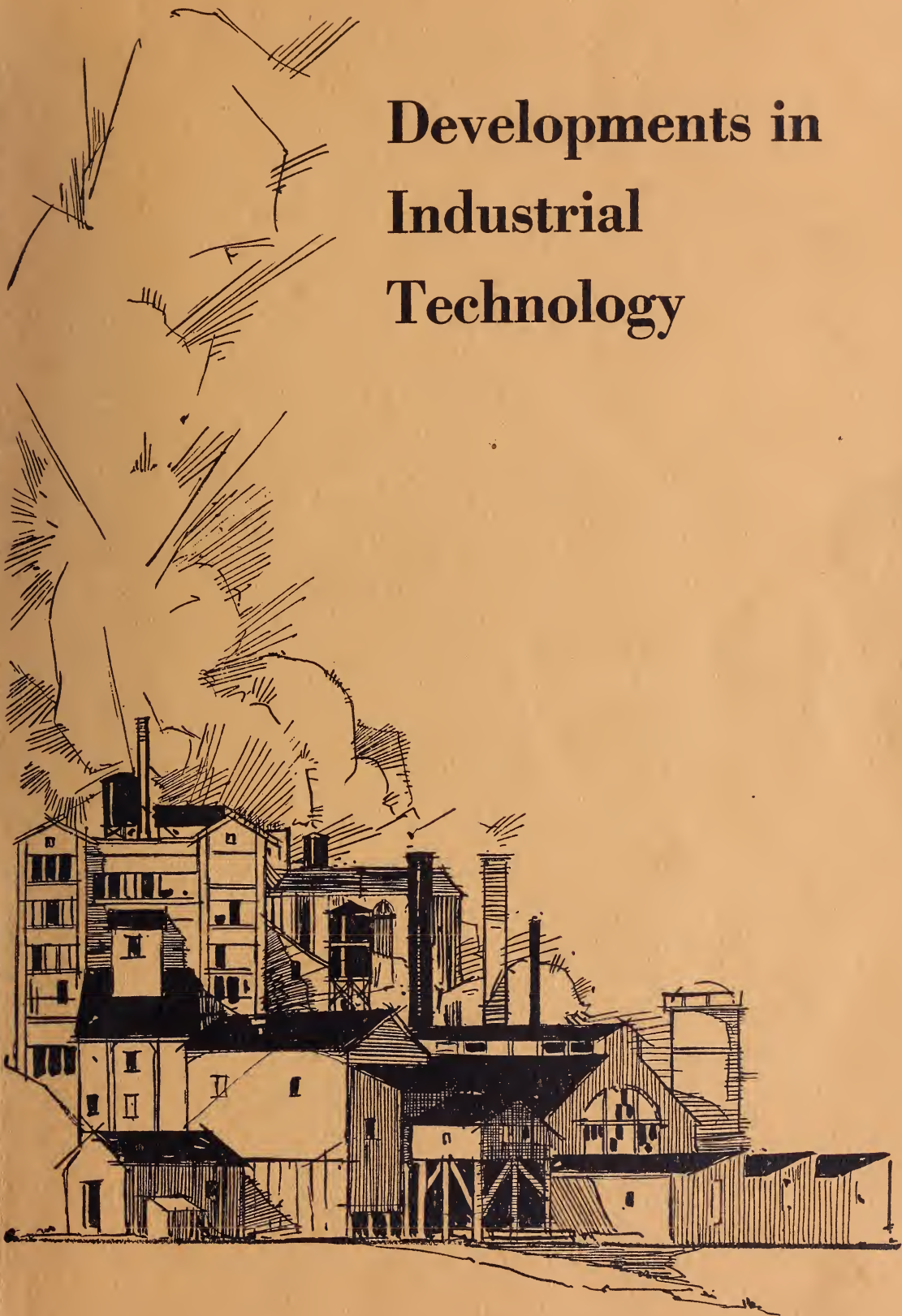


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# Developments in Industrial Technology





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## Separation of Fixed Oils From Soap-Water Emulsions

BY EUGENE E. AYRES, JR.

THE following discussion of emulsions of oils and soap-waters is not based upon any purposed and consecutive research, nor is any reference made to the rather copious literature. Each year the writer comes in contact with hundreds of men, each keenly intent upon some emulsion problem. To ninety-nine out of each hundred the science of colloids and of physical chemistry is exceedingly vague, and yet these men are often successful in solving their problems. They work in the dark, and they are to that extent handicapped, but often the freshest ideas come from those whose points of view are naïve. The following discussion is an attempt to analyze and interpret the collective observations of these "practical investigators."

It is convenient at the outset to make several reservations. Only the types of emulsions encountered in industrial manufacture are included in this discussion. Naturally, it has not been attempted to completely cover the types of practical importance. Zinc and lime soaps, for example, or rosin soaps, or the "soaps," so called, derived by neutralization of organic acids in petroleum, or the soaps of volatile fatty acids—none of these cases is discussed. By "soap" is meant the caustic alkali soaps of the common higher fatty acids. Similarly, the sulphonated fatty compounds and the amides of fatty compounds have been ignored.

### CLASSIFICATION OF EMULSIONS

Simple emulsions of oil and water may be classified as

1. Those in which water is suspended in oil, and

2. Those in which oil is suspended in water.

Many industrial emulsions are not "simple," but may be technically classed as "complex."

A complex emulsion is one in which the dispersed liquid does not consist merely of globules of oil or of water, but in which the suspended globules are themselves emulsions with tiny globules of liquid suspended in them.

Some emulsions are much more complicated in structure than this, especially when suspended particles are ultra-microscopic, but our definition of "complex" emulsions has the advantage of serving our purpose without confusing the issue.

We may make a complex emulsion of the mutually insoluble liquids A and B. The bulk of the mixture is A. The globules suspended in A consist primarily of B, but still smaller

globules of A are suspended in each globule of B. A concrete illustration is found in the emulsion obtained when a saponifiable oil is warmed and agitated with a solution of caustic soda sufficient in amount to saponify only a small proportion of the oil. The oil is the A liquid, and the aqueous soap solution is the B liquid. An example of the opposite type is formed when crude petroleum is thoroughly agitated with two or more volumes of water. Here water is the A liquid, while oil is the B liquid.

A "saturated" emulsion is one in which the globules are packed together as tightly as possible in the space provided by the continuous liquid. If small spheres of uniform size are crowded into a given space, the volume taken up by the spheres will be a definite percentage of the volume of the given space. This percentage is independent of the size of the spheres. But if, in such a system, we should insert smaller spheres in the spaces still available, the percentage will be higher. Mathematically speaking, the function is a variable which approaches but can never reach a limit of 100 per cent. The emulsions met with in practice always contain globules of various size—some larger, and some smaller than average. But industrial emulsions rarely contain more than 50 per cent of the dispersed phase. The writer has never seen an industrial emulsion containing more than 80 per cent of the dispersed phase.

A "dilute" emulsion is obviously one that contains only a small percentage of dispersed liquid. To "concentrate" an emulsion is to separate from a dilute emulsion as much of the continuous liquid as possible, leaving a saturated emulsion.

Concentration of dilute emulsions is practiced commonly in many industries.

### SIMPLE AND COMPLEX OIL-SOAP-WATER EMULSIONS

While the definitions suggested above are still fresh in mind, consider the soap-water emulsion as a type. If the emulsion is simple, the aqueous soap solution is the continuous liquid with the oil suspended as globules. If the emulsion is complex, the oil is continuous with suspended globules of simple emulsion wherein water is continuous. The writer has seen no exceptions to this rule. If we were to take, for example, a liter of oil and agitate with one c.c. of soap solution, the emulsion would be invariably complex. As the oil is



present in such large proportion, the oil is obviously continuous. If the suspended soap-water is separated (say by gravity settling), it will be found that oil globules are suspended in the soap-water unless gravity has also separated the simple emulsion. There are few cases where soap-water can be completely freed from suspended oil globules by subsidence (gravity or centrifugal), while it is a general rule that the continuous oil of a complex emulsion can be freed with relative ease from the suspended emulsions by subsidence.

Take the converse example of one liter of soap-water with one c.c. of oil. This emulsion will always be a simple emulsion.

If an emulsion of oil and soap-water contains more than 80 per cent oil, it is reasonably safe to conclude that the emulsion is complex. If the oil content is below 20 per cent, the emulsion must be simple. The range between 20 and 80 per cent may belong to either class, but in nearly every case up to 50 per cent it will be found that the emulsion is simple.

Without recourse to microscopic examination it is easy enough to determine whether oil or water is continuous in an emulsion. If the emulsion is miscible with water, water must be the continuous phase of the emulsion. If oil is continuous, the emulsion will be miscible with oil. Of course, there are cases of true emulsoids where we find miscibility with both oil and water, but this discussion has nothing to do with such cases. The true emulsoid must be ruled out forthwith.

For industrial emulsions, a convenient test is to pour a few drops of the emulsion into a beaker of water. If the emulsion diffuses through the water, water must be continuous in the emulsion. In the case of a soap-water emulsion, the investigator may draw one other inference—the emulsion is simple, with suspended globules of oil. If the emulsion does not diffuse through the water, oil is continuous, and in the case of soap-water emulsions, the emulsion is complex with suspended globules of simple emulsion.

#### SUPER-SATURATED EMULSIONS

There are what may be termed "super-saturated" emulsions, which may be described as imperfect mixtures of oil with a simple saturated emulsion. The excess oil is not present in sufficient amount to form a primary continuous phase, and this oil is not globular. Such a mixture is possible only when the emulsion is of high viscosity, for otherwise this excess oil would immediately separate. In the diffusion test, the presence of such oil is indicated by a diffusion of the emulsion proper while the excess oil remains on the surface of the water.

Super-saturated emulsions are very common in the industries, but inasmuch as the recovery of the excess oil is so simple a matter, no reference to super-saturated emulsions will be hereafter made.

#### PERSISTENCE OF EMULSIONS

The continuous oil may be most easily separated from a complex soap-water emulsion when the aqueous phase contains a high concentration of soap. For this reason, when a rancid vegetable oil is refined with caustic soda, it is desirable to employ a caustic soda solution of high strength. Weak caustic soda solutions tend to give complex emulsions in which it is difficult to produce a "break," with subsequent settling of simple emulsion. The strength of caustic soda solution is limited only by refining conditions that have nothing to do with emulsion stability.

Simple soap-water emulsions may contain oil globules of two sorts:

(1) Globules that are "fixed"—that will remain intact as globules until something happens—chemical or physical—to unite them, and

(2) Globules that are temporary—that have been formed by agitation, precipitation or what not, and that will unite to form larger globules that yield readily to subsidence.

The only requirement for the agglomeration of these "temporary" globules from the soap-water is sufficient elapsed time. To agglomerate the "fixed" globules without chemically changing the character of the soap-water is an extremely difficult matter. The writer knows of no instance where such agglomeration is accomplished on a large scale. It is common practice to allow an emulsion to stand in a tank or to pass through a high-speed centrifugal to skim off the oil that can be so separated. But some oil is left behind, and additional subsidence fails to separate it.

#### CHARACTER OF OIL AND SOAP SOLUTION IMPORTANT

What governs the percentage of oil removable and of oil fixed? The biggest factor is the character of the oil. In general a glyceride of a fatty acid has a much higher "fixed concentration" than a liquid hydrocarbon. It is possible to incorporate permanently more olive oil than lubricating oil with any given soap solution. But there are some miscellaneous oils and greases and waxes of vegetable or animal origin that give a higher fixed concentration than the fatty acid vegetable and animal oils and fats. Examples may be found in certain constituents of wool grease and in the organic "impurities" in crude vegetable oils. The fixed concentration of any commercial oils as a whole is much the same as the fixed concentration of its worst com-

ponent. For instance, a little linseed oil dissolved in kerosene will raise the percentage of permanently emulsified impure kerosene almost to the value of linseed oil itself. The trace of organic impurity in crude cottonseed oil makes the latter an easily emulsified oil.

In many cases the fixed concentration is coincident with the saturation point. This is not true of any pure glyceride and even less of any pure hydrocarbon.

Next in importance among the factors involved in fixed concentration is the character of the soap solution. This involves soap concentration, the kind of soap, alkalinity, electrolytes and protective colloids. The lower the soap concentration and the alkalinity, the lower the percentage of permanently emulsified oil. The effect of alkalinity on emulsions of easily saponifiable oils may not be readily noted because of saponification reactions. The effect of electrolytes is erratic and will be discussed later. Soluble electrolytes are of course limited to salts of metals of unit valence because of the insolubility in water of soaps of metals of higher valence. Little difference has been noted between various pure soaps, but commercial soaps differ because of the effect of non-fatty-acid impurities. A trace of a water-insoluble soap (zinc or calcium) may or may not increase the fixed concentration.

The fixed concentration is not greatly influenced by temperature.

#### STABLE EMULSIONS

When all "temporarily emulsified" oil has been permitted to agglomerate and separate, the residual soap-water emulsion at its fixed concentration of dispersed oil is regarded as a stable emulsion. The stability is of two kinds:

(1) A resistance to agglomerate, or the merging of globules (with accompanying subsidence) to form a continuous oil phase; and

(2) A resistance to a concentration of the emulsion, or the subsidence of globules intact to produce on the one hand a saturated emulsion, and, on the other hand, soap-water with appreciably less oil in suspension.

The stability of emulsions is regarded as a phenomenon of surface tension, and reactions that affect surface tension will likewise affect stability. But it is an odd fact that reactions which diminish the tendency for globules to maintain their uniform distribution throughout the soap-water medium will usually increase their resistance toward agglomeration. The conspicuous example of this interesting effect is found in soap-water emulsions of increased alkalinity. The higher the alkalinity (caustic soda or normal sodium carbonate, for instance), the less likely we are to succeed in breaking down the globular formation to ob-

tain continuous oil, but the more likely we are to concentrate the globules intact to form a saturated emulsion. Generally speaking, it is much more difficult to agglomerate in a soap-water emulsion than it is to cause a separation by subsidence of globules. It is believed that this is a highly important item to keep in mind. Chemists have been too often accustomed to measure the success of an expedient for separation by the yield of free oil without taking into account the changes that may have taken place in concentration. This naturally arises from the fact that oil is easily recognized from appearance, while emulsions more or less concentrated look much the same. As a case in point, we may quote the following procedure:

A certain soap-water emulsion contained 10 per cent of oil at its fixed concentration. On standing for ten hours, samples of the emulsion from the surface and from the bottom analyzed a uniform oil percentage (because the viscosity was too high for appreciable gravity subsidence in the allotted time). One per cent of caustic soda was added. After standing one hour, no free oil had appeared, but the liquid at the bottom was relatively clear, while the supernatant liquid was thick and opaque. The clear soap-water was drawn off and tested. It contained less than 0.5 per cent oil. The concentrated emulsion was mixed with a quantity of 1 per cent aqueous solution of caustic soda equal to the soap solution withdrawn, and settled again for one hour. No free oil appeared, but a subsidence of globules again took place. After a third similar treatment, the concentration of emulsifying agents had been reduced to such a low point by the successive dilutions that the globules agglomerated and a fairly complete yield of continuous oil was obtained.

Needless to say, such a procedure is impractical for saponifiable oils because of losses of oils by saponification. But though, for this reason, yields are necessarily low, separation is almost as effective as with unsaponifiable oils, in spite of the maintenance of a relatively uniform soap concentration (by saponification). This is because a high fixed concentration is not possible with pure glycerides and soaps, and involves the presence of impurities.

In the commercial soap-water emulsion, the most common emulsifying agent is material that, although unsaponifiable (in the sense that fatty acid soaps may not be formed), is clearly acted upon by alkalis to form a substance colloiddally "soluble" in water. These substances are regarded as "protective colloids." There are a number of protective colloids that either do not occur commonly, or



else are so invariably associated with unsaponifiable greases as to lose individual significance. Such substances are glue, gelatine, albumen, lecithin.

#### TEMPORARY GLOBULAR DISPERSION

To refer again to the "temporarily" emulsified globules, when agglomeration and attendant subsidence have proceeded as far as possible under the influence of gravity, an application of high centrifugal force will not cause additional agglomeration. A force higher than gravity will cause a correspondingly more rapid subsidence of agglomerated "temporary" globules, but the fixed concentration remains the same.

Similarly, an emulsion at its fixed concentration (or below) is favorably affected in one way by high centrifugal force—the subsidence of globules is more rapid. It is an interesting fact that the only variable in practice is in the rate of concentration. If the force is increased or diminished, the rate of concentration is correspondingly increased or diminished, but the residual emulsion is likely to be neither more nor less dilute, and the concentrated emulsion is likely to contain neither more nor less oil. In other words, for any given emulsion, the eventual yield is practically constant if the time during which centrifugal force (or gravity) is allowed to act is commensurate with the force applied. In order to increase the rate at which this yield may be obtained, it is sufficient to increase the force, but to increase the yield we must change the emulsion itself.

#### INCREASING THE YIELD

There is but one change that will increase the yield, and that is an increase in the size of the globules that remain in the dilute residual emulsion. In our use of the word "agglomeration" we have heretofore implied the union of globules to produce a continuous phase. However, agglomeration does not necessarily imply the production of a continuous phase. Almost any physical or chemical change in an emulsion will cause a change in the average and the minimum size of suspended particles, and this change is brought about by the union of several globules or else the splitting up to form smaller globules. It is only under peculiarly favorable circumstances that the change will go all the way to the limiting conditions of continuous oil on the one hand or "soluble" oil on the other hand. Ordinarily the change proceeds only part way—the globules become a little larger but they remain globules, or the globules become smaller but do not approach near enough to molecular dimensions to yield a transparent emulsoid.

#### ELIMINATION OF PROTECTIVE COLLOIDS

The most important factor in securing this partial agglomeration is a reaction to destroy the effect of the protective colloid. The reaction may not destroy the colloid itself, but it is sufficient to throw the colloid out of aqueous solution either by precipitation or extraction. Extraction may be accomplished by rendering the colloidal substance soluble in the oil of the emulsion. An impurity in the oil phase of a soap-water emulsion does not act as protective colloid. Agitation (within reasonable limits) tends rather to increase than to diminish the size of globules in a soap-water emulsion—an effect comparable to the production of butter from cream by churning. The addition of water will increase the size of the smallest globules.

The simplest chemical methods of causing agglomeration are based on the tendency of weak acids to "decompose" the alkaline protective colloids without splitting the soap. Carbon dioxide and boric acid are examples. The impurities when acidulated dissolve in the oil and thus greatly reduce the stability of the emulsion. It is natural to expect that the oil, when finally recovered, will be tainted with these impurities.

Any treatment based upon the elimination of the protective colloid is likely to be limited in its efficiency to the fixed concentration of the pure oil with a pure soap solution.

A condition that reduces the degree of dissociation of soap in solution will still further increase the yield of oil. As an example of such a condition the laboratory test may be cited where alcohol is added to a soap-water emulsion to facilitate the separation of a petroleum-ether extraction.

#### GELATINOUS EMULSIONS PERSISTENT

Commercial soap-water emulsions commonly tend to gelatinize. Pure soap solutions will gel when the soap concentration is high enough, but the gel is rather unstable—a little addition of water or a moderate elevation of temperature is likely to destroy the gel to form a liquid of relatively low viscosity. The gels formed by many commercial soap-water emulsions are more stable. The emulsion is likely to retain its gelatinous character even after considerable dilution with water or the application of boiling temperatures. The stability of the gel appears to be largely influenced by the proportion of protective colloid present, for the non-fatty-acid greases in alkaline aqueous solution form persistent "semi-gels" not so rigid as a pure soap gel but much more stable. The impure industrial emulsion when gelatinous usually has this same persistent semi-gelatinous consistency.

The gelatinous character of an emulsion



must be regarded as important in view of the fact that agglomeration to form a continuous oil phase and concentration of globules to form a saturated emulsion is impeded by high viscosity. The viscosity of these "semi-gels" is gradually reduced as the temperature is raised, but even when boiling, the emulsion is likely to retain gelatinous characteristics. The semi-gel can be truly liquefied only by dilution with water or by chemical action. When sufficient water has been added to eliminate gelatinous characteristics, the viscosity of the emulsion is not greatly influenced by temperature changes. The diluted emulsion will usually remain liquid under any circumstances of physical change, though a chemical change (such as that induced by the addition of a little salt) is likely to throw the emulsion back into the semi-gelatinous state. Conversely, when it is attempted to liquefy a gelatinous emulsion by chemical means (instead of dilution with water), the liquid state is likely to be quite unstable, and a reversion will occur with almost any physical change, such as heating or cooling, agitation, addition of small amounts of water, etc. The addition of a trace of mineral acid to a gelatinous emulsion will often cause liquefaction. A little agitation will restore the gel. Another trace of acid again liquefies, and another agitation again causes reversion. This cycle may be repeated until the soap is nearly or completely decomposed.

A complex soap-water emulsion is rarely gelatinous, for the dispersed phase, when gelatinous, will readily settle out, yielding the excess of oil and the simple emulsion.

#### EFFECT OF DILUTION

Unless carefully prepared, a gelatinous soap-water emulsion will not contain its oil as suspended globules because the viscosity of the continuous soap solution is too high to permit interfacial surface tension to act. The oil will be in irregular streaks or strata. As soon, however, as the emulsion is liquefied by dilution or by other means, the oil assumes its globular form. In one sense, dilution reacts unfavorably on separation procedures, for dilution increases the stability that resists agglomeration. A gelatinous emulsion that will slowly yield up some of its oil in continuous form by agglomeration and subsidence will not yield this oil after dilution. In other words, some of the oil that is "temporarily" emulsified in the gel assumes the state of fixed globules when water is added. To reduce the percentage of oil permanently held up in gelatinous emulsions has been the subject of many a research.

It has been stated that when the concentration of soap, alkali and protective colloid

is reduced, the fixed concentration of emulsified oil will be reduced. Whether or not dilution will cause a separation of oil from an emulsion depends, obviously, upon the mathematical structure of the function involving the variables of dilution and fixed oil percentage. To illustrate, suppose we take an emulsion which contains 10 per cent soap and 20 per cent fixed oil and 70 per cent water. The actual concentration of substances in the aqueous phase will therefore be 14.3 per cent soap, and 28.6 per cent oil. To 100 g. of this emulsion we add 70 g. water. The soap and oil concentrations will be cut in half—7.15 per cent soap and 14.3 per cent oil. If 14.3 per cent represents the fixed oil concentration for this diluted emulsion, we can recover no oil. If the fixed oil concentration is below 14.3 per cent, we can recover some oil. Suppose the value is 10 per cent. The fixed oil in grams will amount to 17. Our recovery will be 3 g., or 15 per cent of theoretical.

Often the fixed concentration will be reduced by larger differentials than the soap concentration up to a certain point beyond which the relation is reversed. The following table illustrates one case. The emulsion was composed as in the above paragraph. The emulsion was progressively diluted, and subjected to a given centrifugal force for a given period. The oil not recovered was regarded as "fixed."

Percentage of Aqueous Phase		Percentage Recovery Per Cent
Soap Per Cent	"Fixed Oil" Per Cent	
14.30	28.60	0
7.13	10.10	15
4.80	5.40	35
3.55	1.95	70
2.80	4.10	25
2.40	4.80	0

The above is an unusual case in that the dilution yielding maximum recovery is so low.

#### RECOVERY OF OIL BY ACIDULATION

The common method in our industries of recovering oil from soap-water emulsions is to acidulate. The acid reacts with the soap to produce fatty acids and the acid reacts also with the unstable alkaline organic impurities (when these are present). The impurities when acidulated are no longer protective colloids, but are usually quite soluble in oil and in fatty acid. When a commercial soap-water emulsion is acidulated, therefore, the recovered material consists of the mutually soluble oil, fatty acid and certain organic impurities that may have been present in colloidal solution in the soap-water. We have seen one case in which the alkali-soluble non-fatty-acid material comprised more than 20 per cent of such an acidulated mixture.

The subsidence of the water-soluble materials upon acidulation is usually rapid and complete because there exists no longer any soap or any alkaline protective colloid to stabilize the emulsion. Occasionally we run up against stubborn emulsions of fatty acid with dilute mineral acid, but these emulsions are totally different from the soap-water emulsion which constitutes the present subject for discussion. In cases where there is a tendency to form stable fatty-acid emulsions by the acidulation of soap-water emulsions, the stability depends very largely upon the physical conditions under which the acidulation is conducted. This is particularly true when the alkali-soluble impurities form oil-insoluble solids when acidulated (wool-scouring liquors).

When it is considered satisfactory to obtain the mixture of oil, fatty acid and impurities, the acidulation of a soap-water emulsion is the obviously correct procedure—inexpensive, complete in yield and uniform in operation. The major reason, in fact, that acidulation is considered unsatisfactory is that methods of separation of oil, fatty acid and non-fatty acid grease, each free from the others, have not received sufficient attention from chemists. The recognized methods for such a separation have involved new soap-water emulsions and yields are negligible.

#### SALTING OUT PROCESSES

It is common knowledge that salt tends to throw soap out of aqueous solution. The higher the salt concentration the more complete will be the precipitation. Solutions of the soaps that are most easily salted will dissolve salt in low concentrations, without any actual precipitation. These low salt concentrations are interesting. Suppose we take a stable emulsion and add enough salt water to bring the salt concentration to 0.5 per cent of the aqueous phase. The usual effect will be the increase of stability. It will be more difficult to agglomerate globules or to concentrate globules without agglomeration. When a high concentration of salt is used, the soap will be thrown out of solution, and the oil may or may not be recoverable. This point is enlarged later on.

#### BREAKING AN EMULSION WITHOUT PRECIPITATING SOAP

But there is a certain point in salt concentration where a soap-water emulsion may be completely broken without an actual precipitation of soap, and the oil may be recovered as a continuous phase. It is believed that every soap-water emulsion (if not too viscous) will yield up some of its oil if exactly the right percentage of salt is carefully added, but the procedure is likely to remain an impractical laboratory curiosity on account of

the difficulty in formulating any rule by which the correct salt percentage may be estimated. A series of tests on three commercial samples of cotton-seed oil soap-water emulsions of nearly the same constitution in oil, soap and water gave the following salt concentrations as necessary for oil recovery—2.1 per cent, 3.6 per cent, 1.2 per cent. These concentrations are based on the water content of the emulsions. In each case when the salt concentration was increased or decreased by a few tenths of 1 per cent, the stability of the salted emulsion appeared much the same as the stability of the unsalted emulsion. This sensitivity appears to be linked with the tendency for a soap-water emulsion to gel with slight provocation of chemical change. There was no gradual relationship between oil yield and salt concentration, but a sudden change at one definite point.

Moreover, there seemed to be no functional relationship between this point and the percentage of major constituents in the emulsion. A careful research would probably show that the critical salt concentration required to bring about this change is a somewhat complex function of all constituents—in particular the proportion of impurities that constitute the protective colloids. It would be helpful if a simple analytical determination could be devised to show what might be termed "effective alkalinity." Because of hydrolysis, soap solutions are always alkaline; but the alkali is often more loosely combined with the protective colloid than with fatty acid, so loosely, in fact, that it is possible to completely saponify a fixed oil in such an emulsion by the addition of normal sodium carbonate, which appears to displace the caustic alkali from the impurities. The protective colloid acts as a catalytic agent in a saponification of this sort. The non-fatty-acid organic material in colloidal solution may sometimes be extracted from an alkaline solution with ethyl ether or benzol.

#### THE CRITICAL SALT CONCENTRATIONS

The effect of low salt concentrations on one emulsion is shown in the accompanying curve, (Fig. 1), wherein salt concentration is plotted against yield. The emulsion contained 75 per cent of a 25 per cent soap solution and about 20 per cent oil, with about 5 per cent alkali-soluble impurity. The yield figures represent the percentage of oil recovered as free oil based on a theoretical yield of 100 per cent, by subjecting the emulsion to high centrifugal force for a given period. The critical salt concentration is not nearly so sensitive with emulsions of coconut oil soap because this soap is more soluble than others in salt water. To revert to high salt concentrations, when soap is "salted out" the precipitation may occur in



one of two ways—with a film of oil adhering to the soap particle, or with a similar film of water. When a salted emulsion is permitted to stand, or is centrifuged to permit immiscible layers to form, the salt water will be found at the bottom, the oil at the top and the soap particles intermediate. The soap layer is not a liquid layer, but a mass of solid particles with interstices occupied by liquid. Whether this liquid be oil or water will depend upon the character of the precipitation—whether the particles are enveloped by films of oil or of water. The settled system may therefore be considered as composed of only two layers—oil and water—with the soap sludge either in the upper portion of the water or else in the lower portion of the oil.

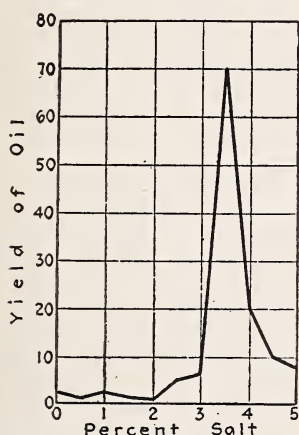


FIG. 1. CRITICAL SALT CONCENTRATION

It is clear that the yield of oil from such a separation is dependent upon the position of the soap sludge. It is highly important that the salting out be accomplished in such a manner as to suspend the soap in salt water. Unfortunately, no generally correct rules can be given here for a proper salting out. The writer has often been unable to secure an aqueous precipitation with some emulsions under any conditions. On the other hand, with other emulsions it has been found an easy matter to so alter the conditions of precipitation as to obtain the soap sludge either in the water or in the oil. An emulsion in which the ratio of oil to soap is high is particularly favorable to the aqueous suspension of the soap. The lower the soap concentration in the aqueous phase, the more likely the soap may be precipitated in the aqueous phase. The higher the concentration of protective colloids, the more likely the soap will be precipitated in the oil phase.

Often when an emulsion contains a high ratio of soap to oil and an oil recovery by salting out appears impractical, it is feasible

to concentrate the emulsion (after appropriate dilution) by gravity or preferably by centrifugal force and to salt out the saturated emulsion. The saturated emulsion contains more oil, less soap, and less organic impurities than does the original emulsion. But unless the soap and protective colloid concentration has been very materially reduced, it is necessary to dilute the saturated emulsion with fresh water to obtain a good yield of oil. The dilution aids the aqueous soap precipitation. When fresh water is added to an unsuccessfully salted emulsion the aqueous phase is diluted, but the soap still remains in the oil phase. In other words, the soap particles remain enveloped by the liquid originally in contact, no matter what changes are made after precipitation.

Any proper discussion of correct procedure for the addition of salt to a soap-water emulsion would lead us into the general problem of reactions between immiscible liquids. Such reactions are common in our industries, and the problem would seem to offer an interesting opportunity for further speculation and research. It is sufficient to remark here that emulsions sufficiently low in soap and organic impurities can be satisfactorily salted out by the addition of solid salt, if at least 30 per cent water is present in the emulsion. For water contents as low as 25 per cent, better results are secured by agitation with a saturated salt solution. For lower water contents, it is advisable to obtain a more thorough emulsification of brine with soap-water emulsion than can be ordinarily obtained with a stirring arrangement. A high velocity nozzle or a centrifugal emulsifier will accomplish this purpose.

If an emulsion is complex (i.e., contains some continuous oil), a dilution with fresh water will not greatly improve salting out conditions. Whether or not water is added to such an emulsion, a severe mechanical emulsification with brine is recommended.

The above data relate to sodium chloride. Other neutral salts of unit positive valence act similarly but in different degree. Sodium sulphate, for example, although not as effective as sodium chloride in the salting out of soap, accomplishes in general much the same results. A very low concentration of sulphate tends to stabilize an emulsion. Sodium sulphate has also its critical concentration where the emulsion is broken without soap precipitation, but the curve is apparently not as sharp as the curve shown for common salt. The writer has not noted the specific effect of high concentration of sodium sulphate.

When a simple soap-water emulsion is chilled to a point where the continuous water is frozen, some of the emulsified oil is likely

to agglomerate and separate after cautiously melting. This effect has been found to occur in cases of gelatinous emulsions high in soap and oil. The best method of freezing, the best methods of melting, the limiting conditions of emulsion composition and the yields obtainable under correct conditions are not known to the writer.

Simple emulsions of coconut oil give an opportunity of observing the opposite phenomenon. At normal temperatures the suspended oil is solid. No agglomeration of practical interest appears to occur when such an emulsion is alternately warmed and cooled except in cases of saturated emulsions, when a partial recovery may be made.

A mention of electrical separation methods will be in order.

#### ELECTROSTATIC ACTION

The various processes for a.c. and for d.c. current at high and low voltage, developed during the past decade for the separation of emulsions of water with crude petroleum, have proved highly successful in this field where large volumes must be handled at low costs (a few cents per barrel). Different investigators have ascribed different theories for "electrical precipitation," but from the nature of the processes one thing is self-evident—the action depends upon the dielectric property of petroleum, which is invariably continuous in these emulsions. The suspended water is affected by the current in such manner as to cause agglomeration and subsequent subsidence. If an aqueous phase were continuous, the current would be immediately short circuited, and there could be no conceivable agglomerating effect on the suspended dielectric oil.

Unless some entirely different method of electrical precipitation is developed, there

would seem to be no possibility of separating oil by this means from a simple soap-water emulsion. On the other hand, there would seem to be no reason why the suspended emulsion in a complex soap-water emulsion could not be precipitated advantageously by means of a modified form of one of the present types of electric treater, because, in this case, the oil constitutes the primary continuous phase.

Perhaps some enterprising refiner of vegetable oils will some day develop an electrical system whereby an "off crude" may be refined with high yield.

In conclusion, we would call attention to an aspect of the soap-water emulsion problem that must be regarded as extremely important and that would require for proper discussion as much space as we have allowed for this entire article. When salts of multiple positive valence are added to a caustic alkali soap-water emulsion, a reaction takes place between the salt and the soap. The products of this reaction determine the stability of the emulsion.

We have attempted to describe and to define a viewpoint. The really difficult step in the development of a colloidal process is to interpret the problem and when an acceptable interpretation is forthcoming, it is not so difficult to find a satisfactory mode of operation. We believe that some of the data given above is rather more than less correct when applied to cases which we have specifically excluded. But if these data are regarded merely as an interpretation, you will not place any mistaken dependence upon what may have been expressed as a formula or rule. Each problem has its peculiarity, and generalizations are so infrequent that each specific case is likely to add to the sum of interesting but difficultly classifiable information.

## Influence of Gypsum on the Blast Furnace Slags in the Manufacture of Cement

BY EUPHIME BERESLAVSKY

ACCORDING to the German patent No. 159,866, "for the preparation of binding materials such as portland cement, damp granulated blast-furnace slags were mixed with unslaked lime and the dry mixture obtained was reduced to powder. However, experiments proved that by applying this method the hydraulic qualities of the grains of slags can be used only superficially. In order to utilize them fully, the mixture of blast-furnace slags and unslaked lime is subjected to the action of elastic steam, after

which the mixture is ground. Usually it is necessary, before grinding, to dry the mixture, after subjecting it to the action of elastic steam. In order to avoid this, the granulated slags are first subjected to the action of steam separately and afterward are mixed with the necessary quantity of unslaked lime. Thus a dry mixture is obtained, which is reduced to powder without preliminary drying in mills. The powdered product, which looks like portland cement, is then used in the same way as the latter."



As is evident from this brief synopsis, this German patent is a method of obtaining a binding material, which hardens in water, from the granulated blast-furnace slags and unslaked lime.

The general method of producing binding material (slag cement) is based on the addition of the necessary quantity of hydrated lime to the dried and granulated slags. The addition of lime depends upon the coefficient of the co-relation of the sum of alkali to the acids.

According to the above:

Composition of Slags Used	Per Cent	Composition of Cement Produced	Per Cent
CaO .....	41.5	CaO .....	45.4
MgO .....	3.2	MgO .....	2.8
SiO <sub>2</sub> .....	42.0	SiO <sub>2</sub> .....	35.7
Fe <sub>2</sub> O <sub>3</sub> .....	0.6	Fe <sub>2</sub> O <sub>3</sub> .....	0.9
Al <sub>2</sub> O <sub>3</sub> .....	10.8	Al <sub>2</sub> O <sub>3</sub> .....	9.7
S .....	1.5	S .....	1.4
Insoluble residue ...	0.4	Insoluble residue ..	0.5
		Loss on ignition ...	3.6

The tensile strength of this cement:

	Pure Kg. per Sq.Cm.	With Sand (1 Part to 3 Parts), Kg. per Sq.Cm.
After 1 day .....	9.6	...
After 7 days .....	31.2	10.5
After 28 days .....	38.2	24.5
After 3 months .....	...	29.9

TENSILE STRENGTH

The tensile strength of the cement is to a certain degree (2.0 to 2.2), according to Tenmayer, proportionate to the coefficient of the co-relation of the sum of alkalis to the acids. This coefficient of the slag, on which I experimented as above, was:

$$\frac{\text{Al}_2\text{O}_3 + \text{CaO} + \text{MgO}}{\text{SiO}_2} = \frac{9.8 + 42.6 + 1.1}{25.6} = 2.1$$

The slag, preliminarily dried and then ground in the rotary mills, was sifted by me through sieves with 4900 holes per sq.cm.

The average tensile strength (according to Mey) of the normal slag cement should be:

After 7 days .....	14 to 19 kg. per sq.cm.
After 28 days .....	20 to 27 kg. per sq.cm.
After 84 days .....	25 to 30 kg. per sq.cm.
After 210 days .....	29 to 35 kg. per sq.cm.

BREAKING STRESS OF NORMAL SLAG CEMENT

The average breaking stress of the normal slag cement (according to Mey) :

After 7 days .....	105 to 133 kg. per sq.cm.
After 28 days .....	170 to 221 kg. per sq.cm.
After 84 days .....	220 to 260 kg. per sq.cm.
After 218 days .....	240 to 288 kg. per sq.cm.

In general, slag cement has less tensile strength than portland cement; however, in admixture with sand it gives reverse results. The setting of slag cement should not be as

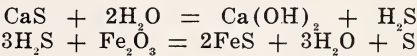
quick as that of portland cement, and in general the process of hardening should be slower. For instance, the Ashland Pozzolan cement begins to set within 3 hours and 40 minutes and finally sets within 8 hours.

Matezius' experiments show that the granulated slag changes owing to the influence upon it of elastic steam in a closed vessel, and the mass crumbles and forms a dry powder—a cementitious and hydraulic product.

Although the conditions and nature of work unfortunately did not permit me to test it, yet I presume that if the process of slaking of lime (producing quick-lime) is done in a closed vessel in connection with the process of obtaining the dry cementitious powder "matezius" from blast-furnace slags, a strong fusing material (stronger than slag cement) will be obtained if these processes are properly carried out. This, in my opinion, requires special attention.

LIME DOES NOT AFFECT HYDRAULIC QUALITIES

The quantity of lime added to the slags has no great bearing on the resistance of cement. There may be added 10 to 25 per cent of the entire weight of dry slag. To a good quality of basic slag 10, 15, 20 or 25 per cent of lime may be added without a noticeable change in its hydraulic properties. I believe that the most suitable coefficient for slag cement is about 1.9. Magnesia, of which there is in slag cement sometimes as much as 30 per cent, does not affect the hydraulicity of cement, although there is an opinion that magnesia in combination with gypsum is the cause of inconstancy of volume of cement solutions. The cementitious solution obtained from slags is of a greenish color, which is explained by the following: The slags contain sulphur in the form of MnS, CaS and CaSO<sub>4</sub> (altogether to the amount of 1 to 3 per cent). When granulating:



FeS gives the slag a greenish color. FeS does not affect the properties of cement; samples of it, having a very dark color, did not change in volume after being kept under water for a long time. On the other hand, in the open air it loses all color and becomes white owing to the oxidation of FeS into FeSO<sub>4</sub>. CaSO<sub>4</sub> does not act detrimentally upon the properties of cement, but merely changes the speed of setting.

The tested granulated slag, which gave by itself, without addition of other materials, a breaking stress of less than 4 kg. per sq.cm. after 28 days, upon addition of quicklime (CaO) gave the following results:

## 90 PER CENT SLAG + 10 PER CENT CaO

Age at Test	Batch Number	Tensile Strength, Kg. per Sq.Cm.
7 days	1	12.9
	2	12.7
	3	13.5
	4	14.0
28 days	1	36.7
	2	36.2
	3	34.5
	4	38.5

Hydraulic modulus 1.4.

Setting of the slag cement obtained begins after 32 minutes.

Final set within 3 to 4 hours.

Normal consistency of the solution is 31 per cent.

## 90 PER CENT SLAG + 2 PER CENT RUSSIAN (GLUKHOZERSK) PORTLAND CEMENT + 10 PER CENT CaO

	Batch Number	Kg. per Sq.Cm.
After 7 days.....	1	14.5
	2	13.9
	3	13.6
	4	14.0

From this we gather that the admixture of a small quantity of portland cement does not affect the strength of the cement.

## BREAKING STRESS

	Batch Number	Kg. per Sq. Cm.
Cube with 10 per cent CaO with sand.....	1	198.6
	2	142.3

## TENSILE STRENGTH

One part (90 per cent slag + 10 per cent CaO) to 3 parts standard sand.

Normal consistency of the solution is 9½ per cent water:

	Batch Number	Kg. per Sq. Cm.
After 18 days.....	1	23.6
	2	23.2
	3	24.1
	4	24.8
	5	20.4
	6	21.4

Storage of briquets—1 day in moist air, 17 days in water.

One part (90 units slag; 2, portland cement; 10, CaO) to 3 parts of standard sand.

	Batch Number	Kg. per Sq.Cm.
After 18 days.....	1	20.3
	2	18.1
	3	19.2
	4	23.0

As shown above, the strength of the mixture of slag with portland cement is even somewhat smaller than without it.

Mixture of 1 part slag + 25 per cent quicklime, hydraul, modul, 1.93.

## THE TENSILE STRENGTH OF BRIQUETS

Normal consistency for 1 part cement and three parts standard sand = 9½ per cent water.

	With Sand		Without Sand	
	Batch Number	Kg. per Sq.Cm.	Batch Number	Kg. per Sq.Cm.
After 28 days	1	150.2	1	284
	2	166.3	2	300
	3	148.7		

One day in moist air, 6 and 27 days in water.

## THE BREAKING STRESS (WITH SAND)

Age at Test	Batch Number	Tensile Strength Kg. per Sq.Cm.	
After 7 days	1	13.6	} About 200 lb. per Sq.In.
	2	12.0	
	3	12.7	
	4	13.8	
After 28 days	1	28.7	} About 400 lb. per Sq.In.
	2	26.7	
	3	26.9	
	4	27.8	

One day in moist air, 6 and 27 days in water.

## THE BREAKING STRESS (WITHOUT SAND)

Normal consistency, 34 per cent water.

	Batch Number		
After 7 days.....	1	27.5 kg. per sq.cm.	} About 400 lb. per sq.in.
	2	26.3 kg. per sq.cm.	
	3	28.0 kg. per sq.cm.	

That is, higher than normal, 20 kg. per sq.cm.

	Batch Number		
After 28 days..	1	50.2 kg. per sq.cm.	} About 650 lb. per sq.in.
	2	47.4 kg. per sq.cm.	
	3	46.2 kg. per sq.cm.	
	4	42.6 kg. per sq.cm.	

That is, higher than normal, 25 kg. per sq.cm.

	Pure	Mixture
After 7 days	About 35 kg. per sq.cm. (About 500 lb. per sq.in.)	About 12 kg. per sq.cm. (170 lb. per sq.in.)
After 28 days	About 45 kg. per sq.cm. (About 650 lb. per sq.in.)	About 16 kg. per sq.cm. (225 lb. per sq.in.)

Thus we can see that the cement obtained from the slags, which I tested, of the Alexandrovsk South Russian Works of the Briansk Co., without sand, was approximately equal in strength to the portland cement, and with sand even exceeded it. The cakes made of this cement had proved the constancy of its volume. Consequently, the above granulated basic slag had proved to be a suitable material for the production of slag cement of high quality.

At the beginning of the activity (1913-1914) of the above-mentioned slag works (reorganized) I had an interview with the director and supervisor of the chemical laboratory of the works and during the interview I stated my plans of working with their slags. In the summer of 1914 this plan was tried in the laboratory of these works, and later on in the shops, and gave good results. In 1917, when I visited the works, they were at the height of their productivity. Wishing to make a further study of the properties of slag and of its interaction with lime and gypsum, I applied the mathematical rule of combination of these elements.

## COMBINATIONS THAT ARE POSSIBLE

The following combinations are possible: Elements:

1. Granulated slag.
2. Non-granulated, or, more correctly, degranulated slag.
3. Lime (quicklime).
4. Gypsum (burnt and semi-hydrus).

Possible combinations of the four elements, in twos ( $C_2^4$ ):

1 and 2	2 and 3	3 and 4
1 and 3	2 and 4	.....
1 and 4	.....	.....

Combinations of the four, in threes ( $C_3^4$ ):

1 2 3	2 3 4
1 3 4	2 1 4

There can be no other combinations.



## FIVE USEFUL COMBINATIONS

Excepting the combinations that are useless for use, 1 and 2, 2 and 3, 3 and 4, 1, 2 and 3 and 1, 2 and 4, we have five combinations, which will serve me for my investigations. If we set aside the combination of granulated slag with lime (1 and 3), already tested, only two binary mixtures remain:

(a) Granulated slag with gypsum.

(b) Degranulated slag with gypsum.

Two ternary mixtures remain:

(a) Granulated slag with lime and gypsum.

(b) Degranulated slag with lime and gypsum.

By "degranulated" I mean the granulated slag, which I had, and in which all granulation properties had been eliminated by means of preliminary heating up to a high temperature and subsequent slow cooling in a closed kiln.

In the fusion of slag and gypsum there can finally take place such a co-relation of the component parts of the combination that it would resemble the so-called "cement bacillus," to which Candlot and Deval have given the formula  $\text{Al}_2\text{O}_3, 3\text{CaO}, 3\text{CaSO}_4, 28.4 \text{ H}_2\text{O}$ . This fusion after hardening of the cement solution produces a large increase of volume. A small quantity of burnt gypsum, on the other hand, acts beneficially. Without altering the volume it retards the setting of the cement and increases its strength.

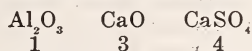
## FINDING MOST FAVORABLE "STATE OF BALANCE"

The retardation of the setting is explained by the fact that burnt gypsum does not enter into interaction with  $\text{CaOH}_2$ . The formation of "cement bacillus" destroys this retarding influence in the setting. The finding of the most favorable "state of balance" of the component parts of the mixture of slag and gypsum is the fundamental problem of our theme. The answer can be given only approximately and as applied to the slag used in the test.

There are indications that by partial addition of gypsum to granulated slag it was possible to obtain a tensile strength of 43 kg. per sq.cm. after 28 days, but the amount of the addition and the co-relation of the gypsum elements to the others I have not been able to determine. From my investigations I would say that the addition of 10 to 15 per cent of gypsum is the most suitable, although I was not successful in obtaining thereby a very high strength in the cement.

Adding from 1 to 25 per cent to our slag we gradually approach Deval's formula, but to reach this formula absolutely, without the introduction of alumina, is impossible, as can be seen from the chemical analysis of the slag

tested. By adding 25 per cent of gypsum the following compound is obtained:



Combinations with this amount of  $\text{CaSO}_4$  (25 per cent) and a little more (30 per cent to 35 per cent) produce negative results.

Thus cubes made of a combination of degranulated slag with 25 per cent of gypsum gave after 28 days a breaking stress of only 63 kg. per sq.cm. and tensile strength of 7.4 kg. per sq.cm. Eight-shapes of the same mixture, but with sand, gave a breaking stress after 28 days of 4 kg. per sq.cm., a slag being used in which granulation had been eliminated by means of preliminary heating up to a temperature of 1280 to 1300 deg. (No. 9 = 10 Zeger pyramid) in a gas kiln and subsequent slow cooling in a closed kiln.

Some of the briquets composed of (1) granulated slag with 5 per cent of gypsum, (2) degranulated slag with 5 per cent of gypsum, placed in water became quite soft after two days, and part disintegrated and turned almost into mud. Those of the briquets that, after remaining two days in a moist place (above water), had not been put in water, but were left for several days in the open air and then for experiment put in water, disintegrated entirely within a few hours.

Samples made of 85 parts of granulated slags to 10 parts of quicklime to 5 parts of  $\text{CaSO}_4$  and 85 parts of degranulated slags to 10 parts of quicklime to 5 parts of  $\text{CaSO}_4$  had swelled, cracked and changed their volumes (just as slags of same composition but with sand) after being in water for 7 days.

## EFFECT OF ADDING GYPSUM

Consequently, slag cement (even with an enlarged hydro-modulus) made of granulated slag and 10 per cent of quicklime, which had, as shown above, a good stress, lost its stress on addition of 5 per cent of burnt (and semi-hydrous) gypsum and also changed its volume.

When I repeated the experiments, keeping to the addition of 4 to 6 per cent of well-burnt gypsum continuously to the granulated slag and slag wherein granulation had been eliminated, the results were the same. After two days the briquets with sand, which had been lying in water, disintegrated entirely, part of briquets (without sand) changed in volume, having swelled and formed large cracks, while the slightest contact broke them up. The final hardening of the samples was sometimes not noticeable even after two days, and a touch of the finger left a mark. Other samples broke up by themselves, not having hardened completely.

With the increase of the amount of gypsum

added up to 10 to 12 per cent of the total weight of the mass, the fusing properties of the hydraulic mixture began to appear thus:

90 parts of degranulated slag to 10 per cent  $\text{CaSO}_4$  (burned) gave the following average:

	Batch			
After 7 days...	1	10.2 kg. per sq.cm.	} Or about 150 lb. per sq.in.	
	2	10.7 kg. per sq.cm.		
	3	10.3 kg. per sq.cm.		
	Batch			
After 28 days...	1	23.7 kg. per sq.cm.	} Or about 350 lb. per sq.in.	
	2	24.2 kg. per sq.cm.		
	3	22.4 kg. per sq.cm.		

When 15 per cent of  $\text{CaSO}_4$  was added to the total weight of the mixture the resistances were about the same. After further additions, however, the resistances in my experiments began to fall. No change of volume was noticeable. Parts of matte cement remained firm and hard and showed no signs of distortion, cracking, checking or disintegration in the steam test for soundness. The beginning and final setting I tested with the Vicat apparatus. Setting commenced on the average after 15 to 25 minutes and final setting took place after a few hours.

#### HOW LIME AND GYPSUM INFLUENCE THE CONSTANCY OF VOLUME AND THE SETTING OF CEMENT

We shall now consider lime and gypsum as factors influencing the constancy of volume and the setting of cement.

According to Dr. Kuhl's report before the Society of German Manufacturers of Portland Cement in 1912,<sup>1</sup> the increase of volume  $\text{Ca}(\text{OH})_2$  during the hydration of the component parts of the cement clinker produces inconstancy of the fusing material. This however, does not always happen. Kuhl's supposition was that the hardened cement has a certain space for the formation of  $\text{Ca}(\text{OH})_2$ ; that is, certain processes take place in connection with the reduction of volume, thereby creating the necessary space for the appearing hydrate of lime. In hardening, one part of the lime changes into hydrate, while the other forms hydraulic silicates and aluminate. These processes act as if in completion of one another and in certain co-relations no change of volume takes place. The resistances within the paste are then equalized by counter forces outside. As is known inconstancy of volume is also the result of a too great content of gypsum. This is considered by Kuhl in the same light as the above in connection with the decrease or increase of volume during the hardening of the cement. The hydrate of the lime in this instance is substituted by sulpho-aluminate lime (according to Le Chatelier  $\text{Al}_2\text{O}_3$ ,  $3\text{CaO}$ ,  $3\text{CaSO}_4$ ,  $28.4 \text{ H}_2\text{O}$ ), or as Micha-

elis calls it, "cement bacillus," formed of gypsum and hydraulic aluminate of lime.

As I have remarked, the inconstancy of volume is caused by the content of too much gypsum; it does not follow, however, that gypsum is always harmful, as it changes the volume in hardening. On the contrary, where there is not a sufficient amount of hydrate of lime to obtain high strength and not all the free space in the thick of the lime is filled by it, the presence of "cement bacillus" is indeed very useful, as it fills up the space remaining empty.

Therefore, reviewing the inconstancy of volume of cement in connection with gypsum, we must consider it as depending not only upon the amount of gypsum itself, but also in a great measure upon the amount of lime in the cement.

Placing the content of gypsum in the cement in connection with the amount of lime, Dr. Kuhl cited a number of examples proving that as a matter of fact, with a low hydro-modulus of portland cements, as for instance, with a hydro-modulus of 1.85, 6 per cent of  $\text{CaSO}_4$  is required, while with a hydro-modulus of 2.3 only 0 to  $1\frac{1}{2}$  per cent is necessary for best strength with no modification of volume.

It is now considered as proved that inconstancy of volume from gypsum depends not on the absolute amount of lime, but upon the relation of gypsum to lime, and that this is especially observed in cements obtained from blast-furnace slags. According to Kuhl, blast-furnace slag granulated in water, with an addition of 3 per cent of gypsum, after 28 days (hardening under water in mixture with sand 1 part to 3 parts) had a tensile strength of 6 kg. per sq.cm. and breaking stress 38 kg. per sq.cm. Owing to the increased addition of gypsum, the 28 days strength of the hydrated samples grew progressively for tensile strength, 27 and 40 and 43 kg. per sq.cm., and for breaking stress, 196 and 412 and finally 604 kg. per sq.cm.

As has been remarked by Kuhl (this has been corroborated by builders in the south of Russia in port construction in the Azov and Black Seas), the relation of cements with poor content of lime to gypsum makes them especially suitable for marine construction; as the cement is the less sensitive to the acid substances of sea water the more gypsum the cement can take in without disturbing the constancy of volume. The more lime is substituted by gypsum, the more suitable will the cement be for marine construction.

Cements that require considerable amounts of gypsum (10 per cent and more) in order to evidence good properties become immune from the destructive action of sulphuric acids; they are inoculated, so to speak. The cor-

<sup>1</sup>Russian Journal "Cement," Vol. 1, '914.



responding action of the gypsum that forms subsequently will be the weaker according as more gypsum is contained in the cement originally.

#### CONCLUSION

Cement prepared with a corresponding correlation of gypsum and slag and properly prepared can be used in the construction of quays, cisterns, reservoirs, canals, bridge supports, etc. When used for molding stones and artificial marble, which may break by rapid drying, they should at first be moistened.

In conclusion I wish to mention the following additional points:

1. Various cements obtained from blast-furnace slags, when they are the most important component parts (in per cent) of the raw material obtained, cannot and shall not be accepted on the general rules applied to ordinary portland cement. For the accept-

ance of above mentioned cements the content of sulphuric anhydride ( $\text{SO}_3$ ) in them must be found in a quantity of more than 2 per cent and even in higher quantities in order to secure their physical and mechanical properties and their resistances, as demanded by the standard regulations for portland cement.

2. A change of this sort makes it possible to utilize properly, without endangering the strength of the buildings, those rather large quantities of slags which have accumulated during the war at the metallurgical works and which cannot be worked into cement in any other way.

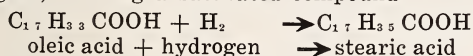
Although such cement would not answer in its chemical composition to the standard international specifications, a very fine and cheap cement could be obtained from these slags if the manufacture of it is properly organized.

## Technical Application of Hydrogen in Hydrogenation or Hardening of Oils

BY HARRY L. BARNITZ

Consulting and Construction Engineer

VERY extensive use of hydrogen has developed in connection with the fat industry. By the introduction of hydrogen into fatty bodies and oils of low melting point these are converted into hard fats of higher melting point. In other words, oils which are composed of unsaturated acids, such as oleic acid and their esters, will combine with hydrogen in the presence of a suitable catalytic agent, forming a saturated compound



Fatty vegetable and animal oils may be described as consisting of a glycerine part and an acid part. The composition of the glycerine part is constant. The composition of the acid part varies from oil to oil, and is characteristic of any one oil, or of any one group of oils.

Several important vegetable and animal oils contain an acid part having the general chemical formula  $\text{C}_n\text{H}_{2n}\text{O}_2$ . Among these we have coconut oil, palm oil, palm kernel oil, butter fat, lard, tallow, and various 'butters' such as cocoa and mace butters. These oils and fats are characterized by the possession of a thick consistency; that is to say, they have high melting points, or, generally speaking, they are naturally "hard."

A considerable number of important vegetable and animal oils differ from those just discussed, in that their acid parts fail to correspond with the general formula stated, to the extent of two, four, six or eight atoms of hydrogen. For instance, in rape oil, and certain fish oils, two atoms are missing. Four are absent in the acid parts of cottonseed oil and soya bean oil. In linseed oil six atoms are missing, and as many as eight atoms are lacking in certain liver and blubber oils. These oils are characterized by the possession of a liquid consistency.

#### SATURATING UNSATURATED OILS

The acid parts of these oils are termed "unsaturated," for they are capable of picking up and combining with additional atoms of hydrogen. Under normal conditions, hydrogen, even in the nascent state, is quite without action on the fatty oils. To convert an unsaturated oil into a saturated oil has led to much investigation and it has been found that the addition of the hydrogen atoms can be effected if the oil is suitably treated with hydrogen in the presence of finely divided nickel, platinum or palladium. Each of these metals acts as a catalyst, and is left unaltered after the hydrogen has been taken up by the oil.

For the purpose of industry the world's sup-

ply of solid fats is deficient, while the supply of liquid is superabundant. Solid fats of vegetable origin are especially scarce. The hydrogenation process permits us to make good the deficiency by converting some of the superabundant liquid oils into hard fats.

Hydrogen has another advantage which is in some cases even more important than solidification effect. The saturation by hydrogen of the unsaturated bodies renders the oil much less likely to oxidize and rancidify.

#### COMMERCIAL APPLICABILITY OF HYDROGENATION PROCESS TO THE SOAP INDUSTRY

As an instance of the commercial applicability of the hydrogenation process, we may look for a moment at the soap-making industry. Tallow may be said to be the ideal substance for the soap manufacturer to work with, giving the necessary stiffness and texture to soap and yielding a firm soap such as we use daily.

Tallow, however, is expensive, and is obtainable only in limited amounts. Accordingly the soap manufacturer falls back upon some of the harder oils, such as palm oil, palm kernel oil and cocoanut oil. These oils are also expensive and are in increasing demand in other industries. If, on the other hand, the soap manufacturer tries to replace them with one or the other abundant naturally liquid oils, such as soya bean oil or whale oil, his product loses greatly in quality, and is apt to be a soft, sticky mass, unsuitable or unsalable as soap for many purposes. Hardening these oils before using them, he obtains a substance practically identical with tallow without affecting the yield from them of that valuable byproduct of the soap-making industry, glycerine. Therefore the hydrogenation process places at the disposal of the soap manufacturer a wide range of oils which otherwise would be next to useless for his purpose.

These remarks will also apply to the candle-making industry, which also calls largely for fats rather than oils.

#### EDIBLE SYNTHETICALLY HARDENED OILS

Fats are now in demand for margarine and certain other edible compounds to a greater extent than can be conveniently met from natural sources of supply. It is certain that synthetically hardened oils will soon be extensively used for edible purposes throughout the world.

Great quantities of cottonseed oil at present are hardened. Increasing quantities of fish and whale oil, linseed, soya bean, cocoanut, palm kernel, palm and other vegetable oils are also being subjected to the process.

A word of explanation is no doubt desirable with regard to the hardening of cocoanut oil.

This oil is just on the border line between liquid and solid fats, changing from a liquid to a solid state with fluctuations in temperature. All its acid part is not saturated, but contains portions of unsaturated acids. It is therefore capable of absorbing a certain amount of hydrogen, and so becoming harder than normally in this climate, but its melting point is not sufficiently raised to meet the requirement of a butter substitute which will stand summer temperature or the high temperature of countries in the torrid zone. To raise the melting point of the hydrogenated cocoanut oil to that required in lard or butter substitutes a small amount of hardened peanut or cottonseed oil is added, therefore contrary to widespread supposition cocoanut oil is not capable of being hardened by hydrogen to any great degree; in no sense comparable with hardening of such oils as cottonseed, soya bean, peanut and oils of this character. Cocoanut oil is almost saturated, as shown by having an iodine number of less than 10, while, for example, that of cottonseed oil is over 100. The iodine number is commonly used to express the extent to which hydrogen has been taken up by the oil in hydrogenation operations.

#### CHARACTERISTICS OF HARDENED OILS

The characteristics of these hardened oils are white, tasteless, odorless substances of tallow-like consistency. They should all be identical whatever may be the particular oil started with, and in theory and practice such identity seems to be attained, at least in the oils as freshly hardened.

It is customary to harden the oils at the soap works, or wherever else they are to be used or are otherwise employed, with but little interval between being hardened and being treated in industrial processes. The point of importance, therefore, is that certain oils will be hardened before shipment to this country. In the Orient and tropics the process is attracting considerable attention from the cocoanut and soya bean oil producers, the idea being that hardened oils may be shipped and carried without risking loss through leakage, which is a serious item in the shipment of liquid oils for long distances.

The technology of the process is dependent primarily upon two conditions—first, the careful preparation of the catalyst, and, second, the use of very pure hydrogen. A slight variation of procedure may quite readily result in an entire failure to harden the oil.

The catalyst ordinarily used on a commercial scale is metallic nickel prepared in a finely divided state by chemical precipitation. Once made, it must be kept strictly apart from certain other substances, notably air, moisture, sulphur, phosphorus, arsenic, car-



bon monoxide, chlorine, etc. These substances oxidize or otherwise react on the metallic nickel, and destroy its catalytic action, 0.1 per cent of  $H_2S$  being sufficient to destroy the catalytic action of nickel. Certain kinds of fish oils contain sulphur, and if this is not removed before attempting to harden these oils, the sulphur will quickly destroy the activity of the catalyzer. The action of these substances on the catalyst is exercised in three ways. First, it means that the hydrogen used must be very pure and free from moisture and sulphur compounds. Second, the oil to be hardened must be thoroughly free from moisture, which it usually contains when received. Third, in preparing the catalyst a stage is reached when it must be treated and handled out of contact with the atmosphere.

TECHNOLOGY OF THE HYDROGENATION PROCESS

When all the necessary conditions are compiled with, the process is not difficult. The oil with the catalyst (usually the nickel catalyzer is employed in the proportion of 40 to 60 lb. per ton of oil) added is heated in an atmosphere of hydrogen inside a closed vessel termed the "converter." The oil and hydrogen are brought into intimate contact and at the end of  $2\frac{1}{2}$  to 4 hr. the absorption is found to be complete. The temperature at which the work is carried on is of great importance. For any given pressure of hydrogen inside the converter there is a definite temperature which must be reached before the absorption begins. At atmospheric pressure this temperature appears to be about 250 deg. C. In practice such a temperature would almost certainly result in

the hardened oil being discolored. To avoid this, some temperature approximating 200 deg. must be used. The pressure of the hydrogen has to be increased above atmospheric as the temperature is decreased. A normal working condition is a temperature of 170 to 180 deg. C. in conjunction with a pressure of 70 to 80 lb. per sq.in. When the absorption is complete, the oil is run out of the converter, cooled, filtered, and allowed to solidify. A general diagrammatic plan of a modern oil-hardening plant of a working capacity for the treatment of 1,000 lb. of oil per hr., with provision for doubling the output, is seen in Fig. 1. The steam boiler and condenser for distilling the water is placed in the basement and is not shown in the plan.

PREPARATION OF THE RAW OIL

The characteristic of the raw oil to be treated may be thick, for instance, as cocoanut oil, therefore necessary means has to be provided for heating the oil before it is emptied into the storage tanks from the barrels and tank cars when received at the works and the oil in the storage tanks must be kept sufficiently liquid to be pumped on to the next stage.

The means provided for reducing and maintaining the oil in the liquid state consists of steam jets for heating the barrels—the tank cars usually have steam coils permanently installed with threaded connections to attach to the source of the steam supply at the works, the storage tanks have flat steam coils at the bottom. The oil in the barrels is first emptied into a vat and from this vat pumped into the storage tanks. From the tank car the oil is pumped directly into storage tanks.

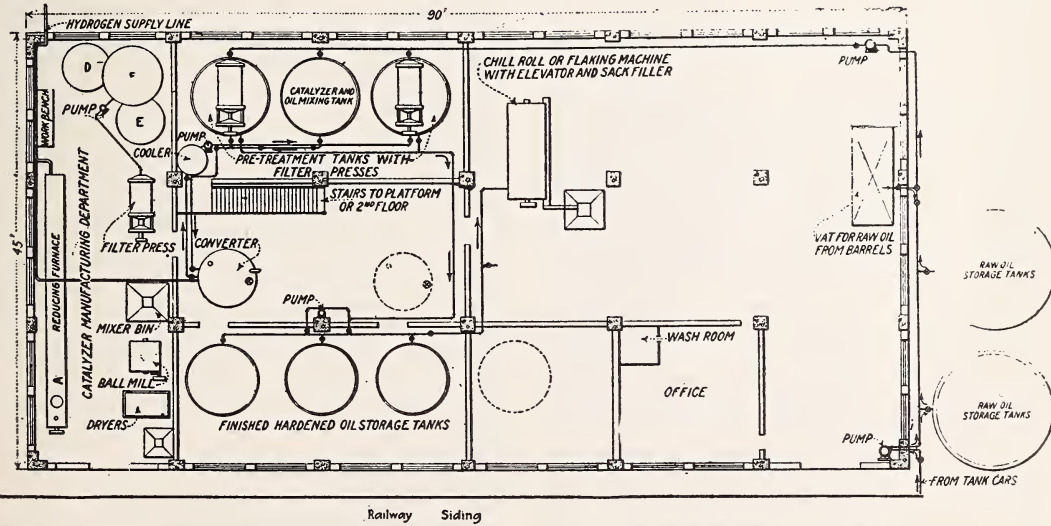


FIG. 1. DIAGRAMMATIC PLAN OF A 1,000 LB. PER HP., OIL-HARDENING PLANT

### DESSICATION OF THE RAW OIL

As the catalyst should not be brought into contact with moisture, it is necessary to extract the moisture from the oil by dessication. This is accomplished in the two pre-treatment tanks. First the oil is pumped from the storage tanks into open circular pre-treatment tanks, having conical bases and fitted with mechanical agitating gear and with steam-heating coils. The oil in them is freed from the moisture. The outlet for the oil is through a valve at the conical base. Steam, fluid level gages, and thermometers are fitted in connection with the pre-treatment tanks. The oil leaving the pre-treatment tanks is mixed with the catalyzer in the mixing tanks and is now ready to be brought into contact with the hydrogen in the converter.

### METHOD OF PREPARING THE CATALYST

There are several methods of preparation of the catalyzer, but the one to be described herein has perhaps been one of the most widely used. In general the catalyst employed is finely divided metallic nickel. It is received at the hardening plant in the form of nickel sulphate in crystals. Its preparation consists of making a solution of the nickel sulphate in tank *D* and another solution of sodium carbonate in tank *E*. Each of these tanks is fitted with an open steam jet to facilitate the preparation of the solution. They are erected over a third tank *F* provided with means for mixing the two solutions when they are turned into it. The result of this mixture is the precipitation of insoluble nickel carbonate and the passage of sodium sulphate into solution. Previous to the admission of the two solutions a quantity of finely divided refractory neutral material is placed in the mixing tank. In practice this material is usually kieselguhr. Its employment is to act as a carrier for the nickel. The mother liquor, the precipitate of nickel carbonate, and the kieselguhr are drawn off from the mixing tank and pumped through a filter press. When the filtering is completed the nickel carbonate and the kieselguhr are found consolidated on the filter cloths as cakes. These cakes are thoroughly dried in hot air driers, and then reduced to powder by means of a ball mill. The carbonate now has to be roasted or calcined in a furnace so as to reduce it to the form of oxide.

The next procedure is the very delicate operation of reducing the oxide to the metallic form. This is effected in a reduction furnace by heating at a certain temperature the oxide in contact with hydrogen, which must be entirely free from air. The furnace employed is either gas-, oil- or electrically-heated and varies in the internal mechanism. Fig. 3 is a diagrammatic sketch of one of the later im-

proved types which is electrically heated and automatically controlled. The furnace *A* is cylindrical in form, and is closed at both ends. It is heated through the under surface at *B*

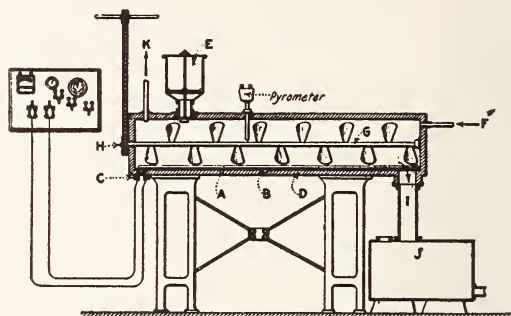


FIG. 3. DIAGRAMMATIC SKETCH OF CATALYZER FURNACE

proved types which is electrically heated and automatically controlled. The furnace *A* is cylindrical in form, and is closed at both ends. It is heated through the under surface at *B* by electrical connections at *C* and incased in heat-insulated material *D*. The pulverized material is fed automatically at the top *E* and the hydrogen is admitted at the end *F* and after circulating through the furnace passes through outlet *K*. Inside the cylinder there is provided a reciprocating worm *G* which is kept revolving slowly by means of the chain drive pulley *H*. The movement of the worm constantly exposes fresh portions of the material to the action of the hydrogen, and also determines the rate of flow at which the material falls through the furnace at *I*. The substance fed to the furnace in the form of the carbonate is calcined to the oxide. After leaving the furnace the reduced material mixed with the kieselguhr must not be permitted to come into contact with the air. It is therefore caused to fall into a tank of oil of the same kind and quality as that to be hardened. This black, oily mixture is ground to a suitable consistency, and is added, with the oil, in the converter.

In the early days the experimenter had considerable trouble with the hydrogenating process. He formed erroneous conclusions, particularly regarding the construction and mechanism of the converter. For this reason there is found a great diversity in its construction.

The secret of oil hardening depends primarily on the activity and uniformity of the catalyzer. Therefore with a highly refined oil and a catalyzer with the properties just stated the oil may be hardened in most any form of converter.

The converter as shown in Fig. 4 is a cylindrical upright tank, closed top and bottom. The lower half is occupied by steam coils; also, during operation, by the oil to be treated, mixed with the catalyzer.

A pump *B* draws the oil from the foot of the converter and discharges it continuously



through a spray onto the oil in the lower half of the converter.

When conditions are properly regulated, the pressure inside the converter, as the hydrogen is pumped in, is seen to rise at first. On reaching a certain point, depending upon the temperature maintained in the oil, the pressure becomes stationary, indicating that the hydrogen is being absorbed by the oil as fast as it is pumped in. By sampling, the degree of hardness is determined, the oil is drawn from the converter through the pipe C, is cooled and filtered. The cooling is not sufficient to solidify the oil, but is only sufficient to prevent the oil from injuring the cloths of the filter press. Practically the whole of the metallic nickel and the kieselguhr is held back in the filters. The pressed cakes of catalyzer left on the cloth are washed and freed from oil, are broken up, and are returned to the catalyst-preparing department, where the material is ready for further use. With a well-refined oil the catalyzer may be used over and over again, for days or weeks. As there are some losses in handling the catalyzer, it is customary to make up for the loss by the addition from day to day of a small amount of fresh catalyzer.

HYDROGEN REQUIRED

The amount of hydrogen required in the hardening of oils varies from 500 to 5,000 cu. ft. per ton of oil, depending upon the nature of the oil, the degree of saturation of the oil and extent of hardening required.

The amount of hydrogen consumption from actual experience on some oils is as follows:

	Cu.ft. per Lb.
Cocoonut oil.....	0.25 to 0.40
Soya bean, corn, peanut, cottonseed.....	1.75 to 2.0
Fish oils (menhaden oil).....	2.0 to 2.5

The amount of hydrogen as given includes that used in making the catalyzer which would be used in the hardening of the particular oil in question.

COST OF HARDENING

ONE TON OF FISH OIL (MENHADEN)

Hydrogen, 4,600 cu.ft. @ \$1.15 per 1000 .....	\$5.17½
Loss of catalyst (nickel sulphate @ \$11.25 per cwt.; kieselguhr @ \$4.12 per cwt.; carbonate of soda @ \$13.34 per ton).....	3.75
Electric current for heating @ \$0.03 per kw.-hr. ....	.30
Power.....	.25
Steam, 1375 lb. @ \$0.85 per ton .....	.58
Water, 450 cu.ft. @ \$0.20 per 1000 .....	.09
Filter cloths, 1 yd. @ \$0.35 per yd. ....	.35
Labor (including preparation of catalyst):	
1 Foreman @ \$0.90 per hr .....	1.70
2 Laborers @ \$0.40 per hr.....	.49
Running repairs.....	
Total.....	\$12.68½

The cost of hydrogen depends upon the manner obtained—for instance, hydrogen can be generated at the hardening plant, it can

be purchased in cylinders and can frequently be obtained as a byproduct. In the latter event the price is very low, considerably less than in the above estimate.

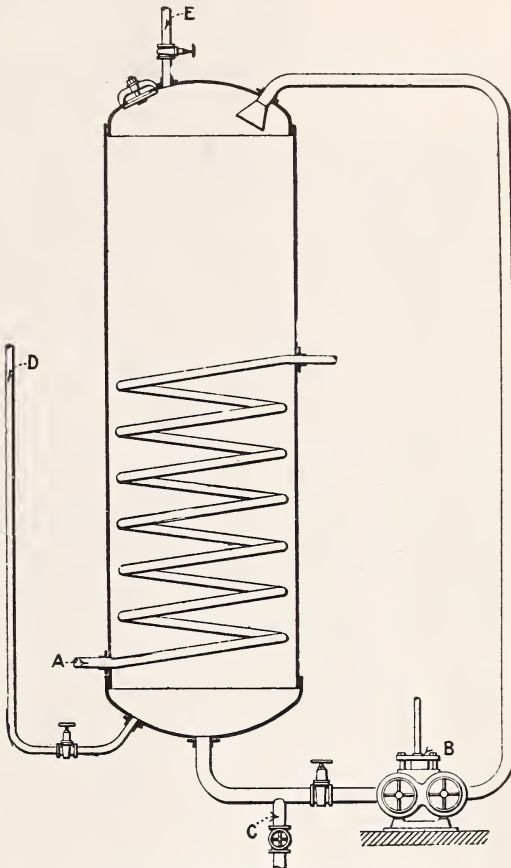


FIG. 4. DIAGRAMMATIC SKETCH OF CONVERTER

It will be noted in the above estimate that this particular fish oil requires more hydrogen to harden it than vegetable oils or most any other oil excepting some certain fish, liver, and blubber oils.

The character of the generating apparatus for the production of hydrogen in relation to the hydrogenation of oils is one of utmost importance, as many factors enter into its proper selection.

The purity of hydrogen is one of importance, but there are factors that are equally as important in other ways to consider. These are:

First. Which particular type of equipment is best adapted to local operating conditions.

Second. Of the various types of the same systems of production, which types are efficient, safe, simple, most economical and conserve long life in operation.

Considerable hydro-generating equipment

has been installed which has not proved satisfactory due to one or all of the above factors. The selection of such equipment

should be left to those who are qualified by technical knowledge and long experience in the field of hydrogen-generating apparatus.

New York City

## Double Pipe Heat Interchangers\*

BY GEORGE A. RICHTER

THE chemical engineer is vitally interested in experimental data giving information on the flow of heat from one fluid to another through metal surfaces. Although many papers have been written on this subject, there is still room for a vast amount of experimental work to confirm established heat laws and to pry further into unknown regions.

George A. Orrok gives an excellent review of published information on conductivity experiments in the 1910 volume of the *Transactions* of the American Society of Mechanical Engineers. Most of the work so summarized refers to the surface condensation of steam, and although some of the deductions listed may be applied directly to a liquid-to-liquid heat interchange, the conclusions reached must be studied with due reservation. A host of formulas have been presented by experimenters for surface condensation. It is very probable that discrepancies in their results do not point necessarily to inaccuracy in work, but may give evidence that there are other factors involved which have not been recognized.

Although the experimental work upon which this present paper is based concerns only double pipe heat interchangers, using hot and cold liquids, a brief résumé of heat transference in general may not be out of place.

### DEFINITION OF CONDUCTIVITY

Heat transference is conventionally expressed in terms of heat units transferred per unit of surface per unit of time per unit difference in temperature. In this country English units are employed. A given system has a certain conductivity ( $K$ ) representing the number of British thermal units transferred per sq.ft. of surface per hr. per deg. difference in temperature between the hot and cold fluid. Mathematically this temperature difference is the logarithmic means of the incoming and outgoing hot and cold liquid:

$$T = \frac{D_1 - D_2}{\log_e \frac{D_1}{D_2}},$$

where  $D_1$  represents the difference in temperature at the beginning of the system and  $D_2$  the difference at the end.

\*Read at the Savannah meeting of the American Institute of Chemical Engineers, Dec. 3-6, 1919.

It is at best exceedingly difficult and probably impossible to cover all cases of such heat transference by means of a few well-selected formulas. A new condenser, or a surface heater of radically different design, always requires experimental investigation in order to learn more concerning the application of heat laws already in existence. Such investigation sometimes involves the fixing of new constants in equations already worked out for other types. Often it means the establishment of entirely new relationships.

### PLANT CONSIDERATIONS

The conductivity, or  $K$ , of a system is a function of the rate of heat transfer in that system. Often the value of  $K$  is all-important in the design of new cooling or heating installations. There are cases, however, where other factors are equally important. In general, the design of a new interchanger involves the following plant considerations:

1. Conductivity, or  $K$ , of various types of units.
2. Capacity of interchanger in total B.t.u. per volume of space occupied.
3. Amount of fluids to be pumped or moved in other ways.
4. Power required.
5. Limiting temperatures of incoming and outgoing fluids.
6. Construction and determining cost of material, practicability, resistance to corrosion, etc.
7. Intelligence required in operation.
8. Physical and chemical characteristics of fluid to be heated and cooled.

Each problem is apt to present other phases for consideration, depending upon requirements. Sometimes one factor of those enumerated above is of paramount importance. Factors 2 to 8 as listed demand the application of engineering sense and judgment. The conductivity factor cannot be calculated from theoretical principles, and consequently most of the experimental work on cooling and heating systems is concerned with that end of the problem.



EFFECT OF VELOCITY OF LIQUOR

If the total cost of introducing or abstracting a given number of B.t.u. in a system is to be minimized, compensatory advantages and disadvantages must be carefully weighed. For instance, the engineer must decide whether it will pay him to raise the conductivity by increasing the velocity of the liquid. In order to make such a decision he must have experimental data showing the effect of liquor velocity on power consumption of pump as well as on conductivity realized. He knows in general that raising the velocity either of the hot or of the cold liquor will increase the conductivity. He also knows this increase in conductivity is not a straight line function of the power consumption involved. The above example is merely one of several which confront the engineer on any new cooling or heating installation. The more data available the less guesswork and worry result.

Several investigators have established equations showing the effect of velocity of liquor on conductivity. Their equations vary quite considerably. In general, they express conductivity as a function of the  $n$ th root of the velocity of liquor. This value  $n$  is usually different for different types of condensers, and consequently an equation cannot be taken without a thorough study of conditions under which this equation was established. Factors of which we have little knowledge may cause very great changes in conductivity with but slight changes in design.

IMPORTANCE OF FILM VELOCITY

For example, we may state with some assurance that the so-called film velocity of water has marked effect on conductivity realized. But what determines film velocity? Tabulated experimental results indicate rather forcibly that a very slight change in design of heat interchanger may cause an almost unbelievable change in conductivity, and

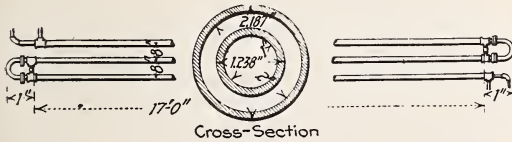


FIG. 1. VIEW AND CROSS-SECTION OF FLAT COIL COOLER

there appears to be no better explanation than that there has resulted a greater film velocity although the average velocity has not been altered. Marked differences in formulas established in the past and in our own work emphasize the necessity of more intense study and further experimental investigation.

SCOPE OF INVESTIGATION

As stated before, the work discussed in this paper concerns mainly the efficiency of so-called double pipe heat interchangers. We were

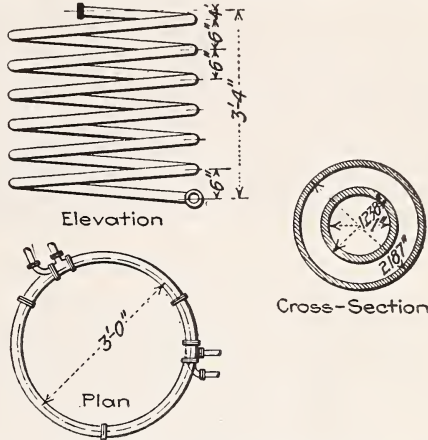


FIG. 2. VIEWS AND CROSS-SECTION OF SPIRAL COIL COOLER NO. 2

interested in a system represented by a liquid-to-metal-to-liquid heat transfer. Inasmuch as the problem involved cooling acid liquors, a lead inner pipe was enclosed in a wrought iron jacket pipe. The procurement of maximum thermal conductivity was necessary in order to conserve lead pipe and to use a minimum amount of cooling water.

Although several designs of coolers were constructed for experimental data, this paper

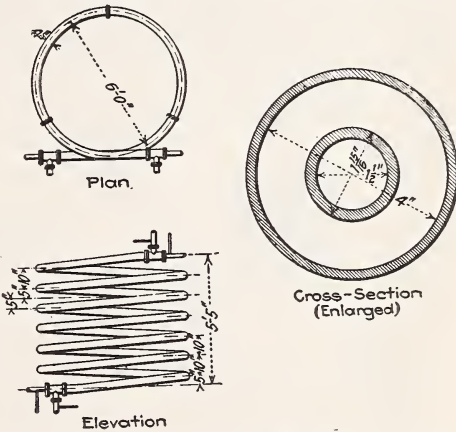


FIG. 3. VIEWS AND CROSS-SECTION OF SPIRAL COIL COOLER NO. 3

confines itself to a comparison of two types, the helical and the straight length. Sufficient data were accumulated to establish direct relationships, which may to a limited extent be used in considering other designs. It is to be noted, however, that although the factors which influence conductivity in these tests

may be used qualitatively for other types of coolers, no quantitative relationship should be assumed.

#### FINAL OBJECTS

Tests were carried out with three objects in view: first, to determine whether a double pipe coil put into the form of a helix would give higher conductivity than one with the same pipe dimensions put into 20-ft. lengths; second, to learn more regarding the effect of varying the diameters of the inner pipe of a helical cooler; third, to study the effect of changing the over-all dimensions of a helical cooler.

#### APPARATUS USED

The units were set up as follows:

1. A 60-ft. 1-in. lead pipe within a 2-in. wrought iron pipe arranged in three 20-ft. lengths. The general assembly and a cross-section of the double pipe is shown in Fig. 1.
2. A 60-ft. 1-in. lead pipe within a 2-in. wrought iron pipe wound in the form of a helix and connected by flanges as shown.
3. A 120-ft. 1½-in. lead pipe within a 4-in. wrought iron pipe flanged and wound in the form of a helix as shown in Fig. 3.
4. A 120-ft. 2-in. lead pipe within a 4-in. wrought iron pipe wound in the form of a helix in exactly the same way as represented by Fig. 3.

Each of these four coolers was set in place in very much the same way. The method for determining volume of liquor, temperatures, and velocities is shown diagrammatically by Fig. 4. Before each test, the hot liquor to be cooled was heated in a tank to the desired

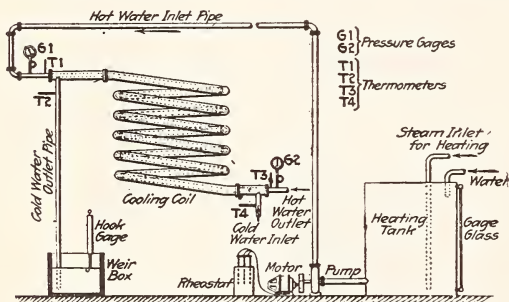


FIG. 4. DIAGRAM OF COOLING UNIT

temperature by means of live steam. The volume delivered during the test was measured directly by drop of the level of the liquor in this tank. Cold water was pumped through the jacket and delivered over a weir for measurement. Pump pressures were regulated by means of a rheostat and thermometers installed at parts needed.

Usually a series of runs was made with

different initial temperatures, in order to determine whether the temperature difference of hot and cold liquor materially influences the conductivity. During the test, readings were taken of the volumes and temperatures of ingoing and outgoing liquor every 30 sec. The first readings were recorded after the system had been operating one full minute, in order to allow time for equilibrium to be established. Knowing the cross-section of lead pipe and wrought iron pipe, the velocities could be calculated.

#### VARIABLES STUDIED

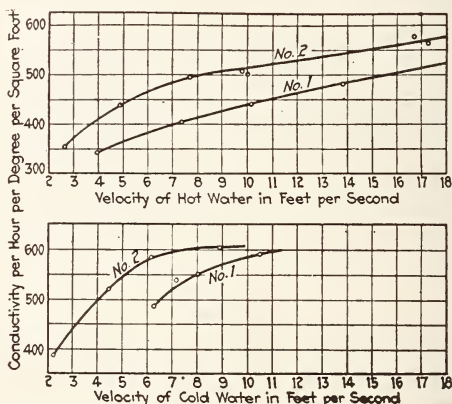
The following factors influencing the conductivity in each case were studied:

1. Velocity of cold jacket water.
2. Velocity of hot water within lead pipe.
3. Change in conductivity due to a change in temperature.
4. Pressure of hot and cold water entering the system.
5. Change in conductivity due to change in design of cooler.

The tabulated results and data obtained in this way are shown by Charts I to VIII.

#### HELICAL VS. STRAIGHT LENGTH COOLER

Chart I illustrates the change in conductivity of No. 1 and No. 2 coolers with change of velocity of hot water, the cold water velocity being held practically constant. Chart



CHARTS I AND II. CHANGE IN CONDUCTIVITY WITH WATER VELOCITY

II pictures the change in conductivity taking place with different cold water velocities, keeping the hot water velocities practically constant. Inasmuch as there is no change in pipe dimensions, the differences in  $K$  represent the effect of curvature in the pipe.

Both charts show a substantial increase in  $K$  as the velocities of liquids are increased. This was to be expected. At corresponding



velocities, the helical cooler gave in each case a higher *K*, indicating that the pipe curvature does increase the effectiveness of heat transfer. Chart II represents runs made with a rather high (17 ft. per sec.) velocity of hot water, and consequently the entire curve lies in a region higher than the curves shown in Chart I, which represents runs with a constant cold water velocity of only 6.1 per sec. Moreover, the curves in Chart II are steeper, showing a greater mathematical change in *K* with change in cold water velocity.

Molier calculated from Joule's researches (*Z. Ver. deut. Ing.*, 1897, No. 6) that the conductivity of heat from liquid through copper to liquid could be represented by a formula (English units)

$$K = \frac{61.5}{\frac{1}{1 + 3.3V_h^{0.5}} + \frac{1}{1 + 3.3V_c^{0.5}}}$$

where *V<sub>h</sub>* and *V<sub>c</sub>* represent velocity of hot and cold liquids respectively. Such an equation means that either hot or cold water velocity increments have equal effects in changing conductivity obtained. This is probably true for some forms of coolers, but is dependent upon the design.

Equations were deduced from the experimental data on coolers 1 and 2 and are put into similar form as taken by Molier's equation.<sup>1</sup>

Cooler 1 (straight pipe).

$$K = \frac{62.7}{\frac{1}{1 + 5V_h^{0.57}} + \frac{1}{1 + 5V_c^{0.57}}} \tag{1}$$

Cooler 2 (small helix).

$$K = \frac{76.2}{\frac{1}{1 + 5V_h^{0.6}} + \frac{1}{1 + 10V_c^{0.5}}} \tag{2}$$

It is to be noted from these formulas that with each cooler an increase in cold water or

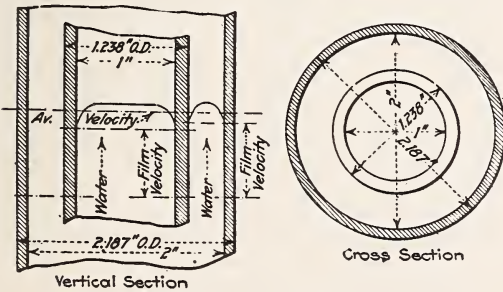


FIG. 5. FILM-VELOCITY IN DOUBLE PIPE COOLER

jacket velocity can have a greater effect in increasing *K* than a corresponding increase

due to a greater actual increase in film velocity of water in the jacket than that obtained by the same increase of average velocity of liquid within the inner coil, and this greater increment may be caused by the obstruction formed due to the position of the inner pipe. In order to get a clear mental picture of this explanation offered, it will be well to consider a sketch (Fig. 5.) drawn to represent and distinguish average velocity and film velocity in the same pipe or tube.

The diagram shows a cross-section of a double pipe cooler, water flowing in the direction of the arrows. The average velocity in

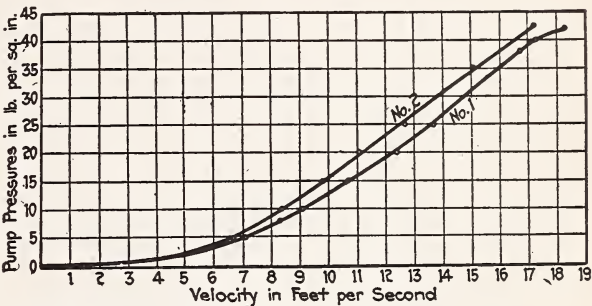


CHART III. VELOCITY IN INNER COILS WITH DIFFERENT PUMP PRESSURES

both jacket and in the coil is equal and represented by a.v. We have reason to believe that it is not this a.v. which determines the *K* of the system, but rather the film velocity, and this f.v. is evidently dependent upon the cross-section of channel as well as the a.v. of total liquid flowing through. Thus, we would state that the smaller the cross-section of the pipe or other channel, the higher will be the actual film velocity for a given a.v. As inferred above, quadrupling the a.v. may increase the film velocity of the inner coil by 2, whereas the same increase of average velocity in the jacket may raise the film velocity of the jacket water by 2.5. We do not know whether *K* is directly proportional to film velocity. If it is, then by reversing the computations used, one could actually calculate the effect of increased a.v. on increased f.v., or solve the equation:

$$f.v. = f(a.v.)$$

In imagining the flow of water through a helical and through a straight cooler, it is not difficult to procure a higher f.v. for a given a.v. in the case of the helical cooler. The a.v. is calculated from actual gallons delivered and does not take into account the path of each particle of water as it travels through the cooler. The helical form would naturally add rotary as well as linear motion and result in greater total velocity of water film next to the surface. The data plotted confirm such

<sup>1</sup>See Appendix for explanation.

a prediction. The conductivities obtained with the helical form of cooler averaged from 10 to 20 per cent higher than those obtained with the straight cooler.

The question of power arises. The rotary motion evidently causes more friction, and would necessitate a greater pump pressure to deliver a given capacity of water. Chart III shows the pump pressure plotted against average velocity with both coolers.

In the operating region of the chart the straight cooler shows a greater a.v. at a given pressure of about 1 ft. per sec. Referring back to Charts I and II, it will be noted that it would require a 4 to 5 ft. difference to compensate for difference in  $K$  found.

There are other analogies and differences which may be pointed out in reviewing the data from which these curves were drawn, only one of which will be considered here. For many years experimenters have made attempts to find relationships of  $K$  and temperature difference in a given system. The curves as plotted in Charts I and II were based on data which include at least four runs at each point, the initial water temperature ranging from 110 to 180 deg. F. A careful survey of the data<sup>2</sup> indicates that in general the  $K$  goes up very slightly with the initial temperature of hot  $H_2O$ . Inasmuch as the initial cold water temperature was held practically constant during any given series, an increase in initial hot water results in a greater average hot water and cold water temperature of both liquids passing through the apparatus. The only explanation we have to offer for a slight increase

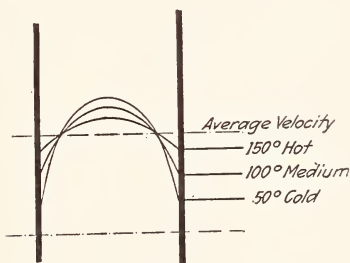


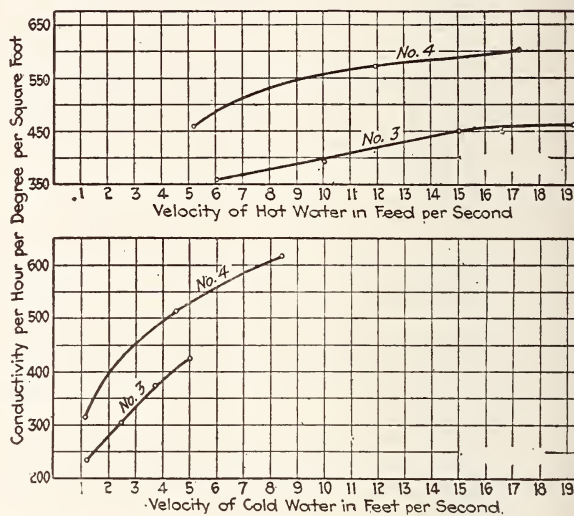
FIG. 6. TEMPERATURE EFFECT ON FILM VELOCITY

in  $K$  with higher average temperatures in the system depends on the fact that the viscosity of water decreases as the temperature is raised. It is probable that the film velocity for a given a.v. increases as the fluidity of the liquid increases, thus allowing greater conductivity. Graphically, we may represent in an exaggerated way the film velocity of water at three different temperatures. (Fig. 6.)

<sup>2</sup>Data were given in Appendix but are not included here.

## LARGE VS. SMALL INNER PIPES IN HELICAL COOLER

As outlined above, work carried out in the investigation allowed us to learn more concerning the effect on  $K$  of changing the diameter of the inner pipe and incidentally to speculate further on factors which influence film velocity. The units employed for the work were larger in size. Cooler 3 consisted of 120 ft.



CHARTS IV AND V. RELATIONSHIPS OF WATER VELOCITIES AND CONDUCTIVITIES

1½-in. lead pipe inside a 4-in. wrought iron pipe in the form of a helix 6 ft. in diameter. Cooler 4 substituted a 2-in. lead coil for the 1½-in. coil. Otherwise there was no difference. Similar series of runs were conducted as in the case of the smaller coolers. Charts IV and V show relationships of water velocities and conductivities.

These charts picture consistently the greater  $K$  obtained with the No. 4 cooler at average liquid velocities equal in each case. The magnitude of the differences rules out all chance of accident or inaccuracy. Our first hope was to explain this increase by some application of the film theory, and although subsequent work may confirm or reject our explanation, we will offer it for what it is worth.

It is reasonable to suppose that an increase in internal pipe diameter will, by contracting the jacket space, increase the ratio of  $\frac{f.v.}{a.v.}$  in

the jacket. Granting this, the greater will be the  $K$ , as far as determined by jacket velocity, as we increase the internal pipe diameter. Conversely, as the inner pipe diameter is in-



creased, we should expect a lowering in ratio  $\frac{f.v.}{a.v.}$  within the inner coil, which in turn would counteract to a certain extent the jacket water ratio. Experimental results apparently prove that this compensating effect is only partial, which means that for a given increase in cross-sectional area of the inner coil, the f.v. increases much more in the jacket than the f.v. decreases in the inner coil.

Chart VI illustrates the changes in average velocity of hot water with change in pump pressure for both No. 3 and No. 4 units. Although no data are available to cover the point, it is reasonable to suppose that similar curves for jacket water velocities would be reversed.

The curves plotted on Charts IV and V may be represented by equations.

$$K \text{ (No. 3 cooler}^3) = \frac{57.5}{\frac{1}{1 + 5V_h^{0.57}} + \frac{2.60}{1 + 10V_c^{0.57}}} \tag{3}$$

$$K \text{ (No. 4 cooler)} = \frac{80.0}{\frac{1}{1 + 5V_h^{0.60}} + \frac{2.60}{1 + 10V_c^{0.50}}} \tag{4}$$

At zero velocity of hot and cold water, No. 3 cooler (by computation) has a conductivity of 15.95, whereas No. 4 cooler would show  $K$  equal to 22.2. It is of interest to note that Molier's equation for zero velocities gives a value  $K = 30.75$ .

SMALL VS. LARGE HELICAL HEAT INTERCHANGERS

In the above we have attempted to draw comparison between a straight pipe and helical

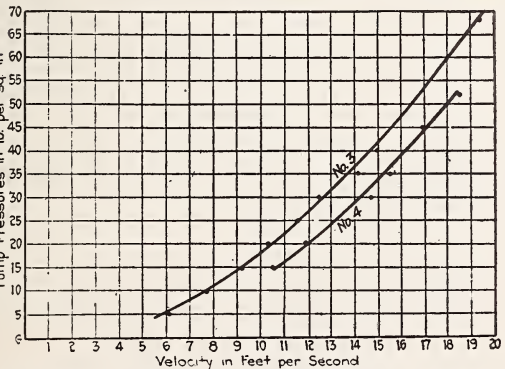


CHART VI. VELOCITY IN INNER COILS AS AFFECTED BY PRESSURE

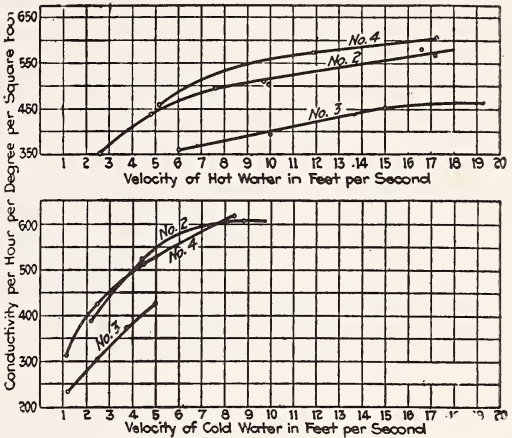
cooler; also between helical coolers of different inner pipe diameters. It may be instructive

to compare results obtained with the small No. 2 helical and large No. 3 and No. 4 helical units.

Charts VII and VIII show the characteristics of these three coolers grouped for comparison.

It is noted that No. 4 cooler gives highest  $K$  values, with No. 2 cooler ranking a close second. No. 3 unit is appreciably lower in  $K$ . The difference in pipe diameters as well as diameter of entire helix makes it difficult to theorize on similarities and differences.

We will, however, tabulate certain relation-



CHARTS VII AND VIII. CHARACTERISTICS OF THREE TYPES OF COOLERS

ships which may throw some light on the subject. If  $x$  = the distance from the inside surface of the jacket pipe to the center of the annular channel and  $y$  = the inside radius of the inner coil, then for each of these coolers:

$$\begin{aligned} \text{No. 2} \dots\dots\dots \frac{x}{y} &= 0.48 \\ \text{No. 3} \dots\dots\dots \frac{x}{y} &= 0.687 \\ \text{No. 4} \dots\dots\dots \frac{x}{y} &= 0.406 \end{aligned}$$

Referring to Charts VII and VIII, we note that the conductivities increase inversely as the ratio listed. This appears to be in accordance with a theory advanced earlier in the paper; viz., that a narrowing in jacket area has greater effect in increasing film velocity than a corresponding enlargement of inner tube cross-section would have in decreasing the film velocity.

Equation 2 and equation 4 show the same close relationship as pictured by the curves covering No. 2 and No. 4 coolers.

SUMMARY

1. A double pipe heat interchanger in the form of a helix gives a marked increase in  $K$

over the same tubular parts put into the form of straight pipe lengths.

2. The film theory may account for this difference in  $K$  obtained.

3. The increase in pump pressure required with the helical unit is small in comparison with the added increase in thermal efficiency.

4. Conductivity in all cases apparently increases slightly with increase in average temperatures in the system. This may be due to an increase in ratio of  $\frac{f.v.}{a.v.}$  as is explained in the contents above.

5. A helical cooler consisting of a 2-in. pipe within a 4-in. pipe gives higher conductivity than a corresponding cooler equipped with a 1½-in. inner coil. A reason is offered for discussion.

6. Conductivities in helical coolers appear to vary inversely as the ratio of distance from inside surface of jacket pipe to center of jacket channel, to the radius of inner coil.

The writer acknowledges with thanks the valuable assistance of Frank M. Jones, who carried on the actual experimental work.

## Appendix

### METHOD

Water was heated to the desired temperature in a large iron tank by means of live steam. A centrifugal pump, motor driven, circulated the hot water; the velocity being regulated by means of a rheostat. The amount of water pumped out of the tank was measured by means of the drop in a gage glass.

Cold water was obtained from the river and its velocity regulated by a valve. Its flow was measured by means of a weir and hook gage.

Temperature changes were observed through four thermometers directly immersed in the flowing liquids. Melted sulphur was used to seal these in the various apertures. The thermometers were placed as near the inlets and exits of the cooler as possible. Runs were made at temperatures approximating 110, 130, 150, 170 deg. Fahrenheit scale.

### DATA ON APPARATUS USED

*Tank*—Height 5 ft. 6 in., diameter 4 ft. 7 in., capacity 677 gal. Water heated by live steam. Graduated water gage on side to measure outflow.

*Pump*—Lawrence, vortex 1½ in. discharge, single side suction, gage 5 in. from discharge to measure pressure.

*Motor*—Westinghouse 5 hp. constant speed, 60 cycle, two phase, 440 volts.

*Weir Box*—Length 12 ft., width 1 ft. 4 in., depth 1 ft. 3½ in.; contracted type, crest length 4.87 in., sharp crested. Channel of approach lined with tin, two vertical baffle plates serving to lessen surging.

*Hook Gage*—Of brass, reading to  $\frac{1}{100}$  in.

*Remarks*—No. 1 straight cooler consisted of three 20-ft. lengths of 2-in. iron pipe containing 1-in. lead pipe. A surface of 36 in. of lead pipe (at the two ends) was exposed to the air and not affected by the cooling water. The under surface of the lead pipe was beaded at intervals to center it.

No. 2 helical cooler consisted of several sections of iron pipe bent to form a helical form. Three sections constituted one turn and were united by flanges. The overall dimensions were 36-in. diameter and 40 in. high. The lead coil was likewise beaded (or provided with lugs) at intervals to center it.

No. 3 helical cooler was similar to No. 2 except that 4-in. iron pipe was used for a jacket; three flanged sections to a turn; nine sections in all (or 6½ turns). The inner lead pipe was not beaded (or "lugged") but merely laid loosely inside the jacket.

No. 4 helical cooler had the same jacket as No. 3 but contained a 2-in. instead of 1½-in. lead pipe.

### CALCULATIONS

*Mean Temperature Difference*.—The logarithmic mean was taken according to the formula (for countercurrent).

$$T = \frac{(t_1 - t_4) - (t_2 - t_3)}{\log_e \frac{(t_1 - t_2)}{(t_2 - t_3)}}$$

where  $T$  = mean T. diff.  
 $t_1$  = initial hot water temperature.  
 $t_2$  = final hot water temperature.  
 $t_3$  = initial cold water temperature.  
 $t_4$  = final cold water temperature.

### CONDUCTIVITY

$K$ , the conductivity constant, or B.t.u. extracted per hr. per deg. F. per sq.ft. of surface, is determined by:

$$K = \frac{A \times B}{T \times D}$$

Where  $A$  = lb. of hot water flowing per hr.  
 $B$  = drop in temperature of hot water ( $t_1 - t_2$ ).  
 $T$  = mean temp. difference.  
 $D$  = sq.ft. of cooling surface.

### VELOCITY

$$V = \frac{\text{cu.ft. per sec. flowing}}{\text{cross-section of pipe (in sq.ft.)}}$$



## WEIR

The weir flow was calculated from the well known Francis formula.

$$Q = 3.33(l - 0.2h)h^{1.5}$$

where  $Q$  = discharge in cu.ft. per sec.

$l$  = width of notch, in ft.

$h$  = height of water above notch level, in ft.

EMPIRICAL EQUATION OF VELOCITY— $K$  CURVE

Since the velocities of both hot and cold water are independently variable, the desired equation connecting  $K$  with water velocity will contain three variables. In the cases in which one velocity was held constant while the other was varied, and then *vice versa*, the relation of hot and cold water velocities to  $K$  can be studied separately. The simplest way to do this is to plot on logarithmic paper values of  $K$  against those of the variable velocity, which tests for a relation of the form  $K = AV^b$ , where  $A$  and  $b$  are constants, or indirectly also for the similar form  $K = AV^b + C$ , where  $C$  is also a constant. In the former case the graph approximates a straight line, in the latter a curve which is concave up-

ward if  $C$  is positive, downward if  $C$  is negative. The experimental data give a graph which is a curve concave downward; this is an absurd result physically, since it means that at zero velocity  $K$  is negative. Another form of equation should be sought.

The form which is suggested by Hausbrand ("Evap. Cond., & Cooling App." Revised Ed., p. 305), namely,

$$K = \frac{1}{1 + 3.3V_h^{0.50}} + \frac{1}{1 + 3.3V_c^{0.50}} \quad (\text{English Units})$$

has been found to satisfy the experimental data quite accurately, given slight changes in some of the numerical constants. An equation as this cannot be directly fitted to data, and a method of "cut and try" until the errors are below the experimental limit of accuracy is the only available method; on this account the constants are mainly round numbers, and the fit is not as close as might result from some method of direct solution.

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## Corrosive Action of Soils on Iron and Lead

BY L. A. STENGER

ONE of the features of industrial conditions little noticed by the average person is the multiplicity of pipe lines, cables, conduits and various other metallic structures found in the subsoils of cities. These structures, with the exception of earthenware sewers and conduits and bituminized fiber conduits, are constructed from cast or wrought iron, steel and lead. The iron and lead are used for water pipes, iron is used for electrical conduits and gas pipes, and lead, usually containing 2 per cent of tin, is used as a protective covering for electric power and telephone cables. Rails of street railways may be included with these structures, also steel foundations of buildings and steel tunnel linings.

Usually these pipes, etc., are placed in the soil with the idea that they will not be affected, at least to the point of destruction, by any corrosive agencies. Attempts are sometimes made to paint or coat the metallic surfaces for protection, more often not.

An enormous amount of work has been done investigating the causes of corrosion of iron and lead in air and the methods for their adequate protection. Comparatively little has been done investigating and preventing corrosion of these metals in soils.

There have been several theories advanced to explain the corrosion of iron. These are the electrolytic, the carbon dioxide or acid, the hydrogen peroxide, the oxidation and the biological or bacterial. From the results of work on this subject, together with a study of the publications of Whitney, Cushman, Gardner, Walker and many others on corrosion in general, the present author believes that practically all corrosion, of both iron and lead, is electrolytic in action.

### CORROSIVE ACTION OF SOIL

The general study of the subject was begun with field observations of underground structures in different places. Extensive work of this type was done at Havana, Cuba, in 1911, by S. T. Todd, of the General Electric Co., and the writer. At the time a new sewer system was being installed, the excavations for which offered a rare opportunity for observing the many piping systems buried in the ground. There it was found the corrosive action of the soil on iron was severe. The most damage was done to the smaller iron gas and water service pipes. From reliable information from several sources, it was found their life was from three to seven years, for either



wrought iron or steel pipes. A poorly galvanized pipe would corrode as badly as a black pipe. A good heavy galvanized coat was an effective protection. Corrosive action was very marked also on cast iron pipe. Careful work was done to find leakage electric currents where this corrosion occurred. None was found. The street railway rails carry practically no current, the double trolley system being in use. The rails of two electric lines entering the city carried current; these were the only sources of leakage current in the city, and, owing to the good soil conductivity, damage from that current would be localized closely to the lower potential points of the tracks. No damage had been reported from this cause. Furthermore, corrosion had been common in that city before electricity had been used at all, therefore it is absolutely certain the pipes were corroded by reactions between soil constituents and the metal.

In Indiana there was laid in 1891 an 8-in. steel gas pipe with screwed wrought iron couplings. This pipe extended from the Grant County gas fields to Crawfordsville, where it ended about one-half mile from an electric railway. This pipe was taken up in 1911. It was corroded in local areas over the pipe, at many places through the walls, and generally over the whole length of the line. It was buried 3 to 5 ft. deep, lying in moist yellow clay soil. This corrosion was also due to reactions between soil constituents and iron.

In Pierre, S. D., cast iron water pipes have been replaced on account of damage due to soil corrosion only. Small iron service pipes were corroded to leakage in six years. The subsoil there is a heavy clay.

Cast iron and steel pipes have been found in Minneapolis and St. Paul, corroded to destruction in black peat soil, cinder fills and clay. These soils were found to be actively corrosive.

Commercial lead is very long lived under ordinary circumstances. However, in Havana it was found that lead covers of some insulated electric cables laid in earthenware conduits were destroyed in three years. This occurred where silt had leaked into the conduits, and where, at times, water ran through them. The lead water service pipes buried in clay were in an excellent state of preservation, and all observations and information indicated that they were undamaged.

#### CORROSION IN ELECTROLYTIC OR AUTO-ELECTROLYTIC

Consideration of these facts and others leads to the classification of corrosive effects into two types. One, called electrolysis, is the resultant of an outside generated electrical cur-

rent flowing from the metal by an electrolytic conduction path. The other has been termed auto-electrolysis; it is electrochemical in nature, and nearly all corrosive effects on subsoil structures, not caused from electrolysis, are produced by it. These two types are to be clearly differentiated, although it has been found that their effects are similar, and as they are so nearly related, any study of corrosion should include consideration of each, especially when corrosion causes are under investigation.

Localized corrosive action on iron, commonly called pitting, may easily destroy gas or water pipes, as a leak is caused in a comparatively short time. The electrolytic theory may be applied to explain such corrosion. Iron has a high solution tension, which causes iron ions to leave its surface under electrolytic conditions, as in moist soils. This ionic travel sets up an electric current. If there is a particle of material electronegative to iron and in contact with it, the current will be directed and will flow from the iron through the adjacent soil to the electronegative area back to the iron. The result will be iron going into solution and becoming oxidized to hydrated iron rust, which is insoluble, porous and an electric conductor. The hydrogen formed by this electrolysis is oxidized to water. If free hydrogen were formed, as in rapid action, the current would be reduced or stopped by insulation due to the gas film on the electronegative area; that is, the miniature battery would be polarized. But it is found by experiment that all the hydrogen is oxidized, and no gas is evolved, and that the action is continuous until the iron is all removed in the immediate vicinity and a pit results. This action is then auto-electrolysis. Any bare iron structure in soil is subject to auto-electrolysis, as the soil will always be more or less an electrolyte, as it contains soluble salts, or acid ions, and moisture.

On account of the number of variable factors found affecting corrosion rates, it becomes rather difficult to isolate and to study them effectively. Considering the metal alone, prominent factors affecting its corrosion rates are constitution, properties of components, segregations, foreign substances including gases, states of strain, solution tension and conditions of surface.

External factors involving the soils and conditions outside of and in contact with the metal are moisture content, gases, composition, electrical conductivity and components. The latter may be chemically corrosive, electronegative to the metal and catalytic in action. Also porosity or density, homogeneity, concentrations, bacterial conditions, temperature and pressure are to be included.

### POTENTIAL EXPLORATIONS

At the beginning of some laboratory work done by the writer under direction of Prof. E. E. Nicholson at the University of Minnesota, some experiments were carried out, electrolyzing cast iron and sheet steel in solutions. They show that the iron goes into solution at a rate of 1.042 g. per amp.-hr., approximately. This is with a valence of two. Further work was then done using several irons in different soils, to compare all effects under the various conditions, and to find the corrosion rates both by electrolysis and auto-electrolysis. For electrolysis in soils many tests were run, using different soils and iron, steel and lead anodes. Tests were made on iron anodes with scaled, smoothed, or polished surfaces. Various voltages and current strengths were used. After deducting for the corrosion due to auto-electrolysis as determined under the same conditions without any applied electric current, the efficiency of electrolysis was determined. From all results, about two-thirds of the iron anodes having an electrolysis corrosion efficiency under 100 per cent gave an average of 81 per cent efficiency. The remaining 33 per cent of anodes at 100 per cent efficiency and over gave an average of 110 per cent. Lead anodes gave an efficiency of from 80 to 150 per cent. From these results no law connecting any of the variable factors with a definite electrolysis efficiency was noted.

Electrical or galvanic phenomena found in connection with auto-electrolysis were studied. Two identical electrodes of copper (platinum could have also been used) were made, and covered with pads of cotton cloth or filter paper. These terminals were connected to a suitable electrometer. Wetting the pads with dilute acid and placing them on an iron surface, an electromotive force was produced. The resulting current was caused by the iron ions passing into solution at a faster rate in one electrolyte than in the other. The effect is also observed after using soil under the terminals instead of pure acid electrolyte. The energy generated is dependent on various factors, and the voltage is due primarily to the solution tension of the metal.

### CURRENT STRENGTH STUDIED

Studies were made of these potentials and the resulting current strengths. A Weston 15-volt voltmeter is a suitable instrument to use for measurement of voltage with electrodes as described about 1 in. in diameter. This instrument does not indicate the full voltage generated, on account of the limited current flow. A special inclined capillary Lippman electrometer was constructed for this work and found excellent. It takes no current and indicates potential up to 0.8 volt accurately.

A Weston milliammeter may be used to measure the current. In making such electrical surveys on bright pure iron, usually the electrode put down first is found to be electro-positive. The current flow would be from the iron under it. Using ordinary moist clay as electrolyte and two similar copper terminals, placing one clay first on pure bright iron, and in a few seconds the other in another place on the same piece of iron, closing the circuit with the copper terminals through the Lippman electrometer, voltage up to 0.1 was indicated. The copper terminals may be reversed, also reversing the electrometer, to determine if there is any voltage due to dissimilarity between them—there should be none. Care should be used to avoid contact between terminals and iron.

With this method, using moist soils as electrolytes, potentials were measured between points on many kinds and conditions of irons found in commercial use. On clean ordinary surfaces would be found 0 to 0.1 volt, clean iron to mill scale 0.3 to 0.5, clean iron to copper 0.8 to 1.0, clean iron to carbon 0.8 to 1.0, clean iron to red rust 0.3 volt. The clean iron would be electropositive in all cases; current would leave it and cause corrosion.

### CAUSES OF AUTO-ELECTROLYSIS

The destructive effects of auto-electrolysis depend upon the electronegative material to a considerable degree. If it is a copper coating with a flaw exposing iron, then under auto-electrolytic conditions a hole will be corroded through the iron in a surprisingly short time. A superficial corrosion will expose the graphitic carbon in cast iron; an area is thus electronegative and the iron ions are removed through the porous electrolyte-saturated soft material, characteristic of corroded cast iron. Mill scale, if thick and unbroken, is a good protection to iron, but if broken becomes a source of danger, since it is electronegative. In soils where the electrolytic conditions are not favorable for corrosion, as in clean sand, action may be suspended indefinitely, only a small amount of rust forming.

### CORROSION OF PUREST INGOT IRON

Pitting will occur in polished, pure irons (analysis 1) in a clean well-mixed clay, due to the same causes with no apparent electronegative areas on the iron itself to direct or localize the reaction. This may be due to either or both the following causes: slight differences in the iron itself, or concentration cells set up in the clay. Using the Lippman electrometer with electrodes of similar metal, preferably small platinum wires, surveys over a piece of moist clay showed potentials of 0.01 to 0.02 volt between different points. Attempts



were made in this way to locate the low potential points on a smooth clay surface. Then a polished, pure iron plate was placed on it. Allowing action to continue a few days, the iron was examined to see if the corroded areas had any definite relation to these low points. Fair correspondence was obtained on one specimen, but others did not give definite results. These potentials are very difficult to locate, but it is probable they aid in starting local actions on the iron surface, producing red rust in small amount. This is electronegative, and action then becomes definite, and pitting proceeds.

A special corrosion cell was used to duplicate conditions of underground structures for further experiments on auto-electrolysis measurements. Three-inch bituminized fiber conduit was cut in sections about 3 in. long and filled with soil, in which was placed the iron plate. Sheet rubber disks placed in the ends made them air- and moisture-tight, and paraffined wooden disks over these completed the cell. With this arrangement, the specimen could be subjected to pressure. Sets were made up to determine the effects of different pressures and temperatures encountered in practice.

#### CORROSION OF LEAD

Lead, having a very low solution tension, is not so susceptible to auto-electrolysis as is iron. External conditions will produce corrosion, however, in a somewhat different manner. If two soils are in contact with a metal, one of which contains a substance subject to

often corrode near the floor line. Cable covers lying in cement ducts and lead pipes in mortar walls are also destroyed. If water from condensation or other sources is allowed to collect or run down or around a lead structure under conditions when soluble salts are present, there will be formed a concentration cell. The electromotive force set up is caused by different velocities of different ions, which would be found in any surroundings of a pipe in cement or soil. The more dilute solution would be the fresh moisture supply; the more concentrated solution would be near the metal surface in the surrounding medium. Common specific instances of this type of corrosive action are seen at the bases of iron poles at the ground line. It occurs also if the pole is set in cement. This is a plausible explanation of the corrosion of the lead cable covers at

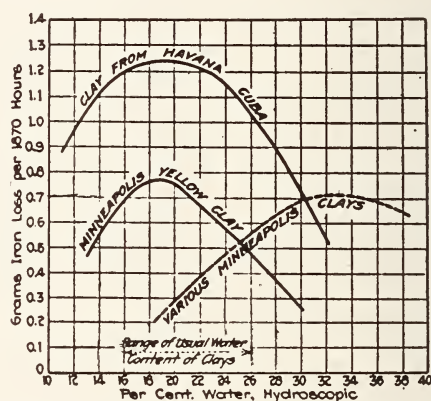


CHART SHOWING VARIATION OF AUTO-ELECTROLYSIS WITH MOISTURE CONTENT OF SOILS

Solid lines for cast iron No. 6. Broken line for both scaled and clean steel No. 3.

No.	1 Per Cent	3 Per Cent	4 Per Cent	5 Per Cent	6 Per Cent	7 Per Cent
Graphite Carbon .....	.....	.....	.....	2.20	3.23	.....
Combined Carbon.....	.....	.....	.....	.73	.41	.....
Total Carbon.....	0.02	0.200	0.060	2.93	3.64	0.153
Si.....	.003	.003	tr.	3.070	1.62	.....
S.....	.005	.041	.019	.051	.133	.....
Mn.....	.011	.432	.365	.283	.324	.....
P.....	.000	.010	.027	.500	.458	.....
Cu.....	.000	.170	.000	tr.	tr.	.233
1. Pure ingot iron No. 16 sheet.						
3. No. 16 sheet.						
4. No. 22 sheet.						
5. From 6-in. cast iron pipe.						
6. Cast iron, cast in $\frac{3}{8} \times 1\frac{1}{2}$ in. strips, broken 2 in. long, for test in soils.						
7. No. 20 sheet.						

a change of valence, we may expect an electrical current flow. This current will enter the metal as part of its circuit, and leave it again, in the near proximity of the bi-electrolytic soil, causing corrosion of the cathode areas. Examples of lead corrosion of this type are given in a paper by E. H. Schofield, Minneapolis, Minn., and the writer, *Electric Railway Journal*, 1914, p. 1092.

Lead is also liable to corrosion from other conditions. Pipes leaving moist cement floors

Havana, previously mentioned. The bottom side of the cover lay in silt, electrolytically more concentrated. The dilute solution would be from condensation and the water flowing intermittently in the conduit, in contact with, the upper surface of the lead.

The complete report of this investigation necessarily carries much detail which need not be included in this review. Tests on approximately 150 soil samples collected in the different cities mentioned, and the fact that many types of iron and lead specimens were treated in these soils, will give an idea of the scope of the work. Some representative results are given in Tables I and II. The influence of the moisture content of clays is shown in the chart, but this also shows that the electrolytic nature is variable in the different clays. Analyses of several soils were made, and it was found that the combined sulphates and chlorides had the greater influence in increas-



ing corrosion. Although the amounts of these components are small in an average soil, and perhaps not over 0.5 per cent in the most active clays, yet their action is remittent and continuous, and corrosion proceeds without renewing the supply of acid ions.

An engineering crime often committed is that of placing iron pipes in cinders. Cinders have carbon particles, sulphates, and carry much moisture. This furnishes a most excellent example for illustration of the electrolytic theory of corrosion, as there is at once formed numerous localized electric batteries, where the iron is the positive and corroded element, carbon the electronegative pole, and the sulphates dissociate and form a very active electrolyte. As a result, the iron pipe is certain to leak, sometimes within a year.

### CONCLUSIONS

Some other conclusions derived from these experiments may be stated as follows:

Electrolysis of underground structures may be caused by certain definite conditions, which may be determined by electrical measurements and a study of the environments.

The electrolytic theory is applicable to corrosion, of underground iron and lead structures

In comparing the corrosive resistance of different types of irons and steels, a careful study should be made of the conditions under which the metals are to be used, and tests conducted under these conditions. Conclusions should not be based on a few experiments, but many tests should be conducted and studied. A good factor for comparison is the "corrosion rate per unit area corroded per year." This factor varies with different metals and with different external conditions, as shown in Table II. Iron specimens should be treated at least 400 hours or longer if possible. The moisture content of the soils in the cell should be maintained constant. The corroded areas usually are definite on the cleaned test plate and may be measured by planimeter.

From experiments performed, and corrosion rates found, the probable life of an iron structure in given soils may be predetermined. The weight of  $\frac{3}{8}$ -in. iron 1 sq.in. in area is 15.8 g. Assuming corrosion forms a conical pit, the metal removed weighs 5.2 g. Referring to Table III, the scaled mild steel specimen in clay showed a yearly corrosion rate per square

inch of corroded area of  $\frac{5.2}{0.51}$  is 10.0 years, this is the probable life of a mild steel black iron pipe with  $\frac{3}{8}$ -in. wall, buried in an average moist clay soil.

The ordinary coatings, mill scale, poor grades of galvanizing, casting skin and tar

TABLE II. IRON LOST FROM CORROSIVE ACTION OF NATURAL SOILS

Cast Iron (Anal. 6)		Mild Steel (Anal. 3)		99.94% (Anal. 1) Ingot	
As Cast	Polished	With Mill Scale	Polished	Sheet	Polished
A	B	A	B	A	B
Soil—Clay 21.5% water					
2.02	1.18	1.36	0.90	0.83	0.41
				0.992	0.34
				0.47	0.12
Soil—Black Peat 39.4% Water					
2.75	1.05	3.44	2.65	2.22	2.47
				1.70	0.57
Soil—Mixed 27.8% Water					
1.48	1.18	2.40	1.60	1.29	0.807
				0.84	0.45
1.34	0.64			1.06	0.59
Soil—Loam					
1.51	0.66			0.97	0.52
Soil—4-in. pipe in clay and black peat					
171	5.18				
171	5.18				

Column A, grams per year lost from plates; column B, grams lost per year per square inch of corroded area. Area of plates 4.8 to 5.5 sq. in. Plates underlined treated 1.07 years; all others 0.23 year. The 4-in. cast iron pipe, 41.5 in. long, was treated 0.85 year. Cells in glass beakers. Large pipe in wooden cell. Loss by water evaporation determined by weighing cells at intervals and replaced by adding pure water.

dips on cast iron have little value as protection against auto-electrolysis, and in cases accelerate it. Tar dips lengthen the life of cast iron by delaying the action, but the coating will soon fail in spots.

The longer life of cast iron is due to its greater wall thickness.

Corrosion rates of iron are little affected by temperature changes within the range usually found about water pipes.

Corrosion rates are appreciably increased by

TABLE III.

### AUTO-ELECTROLYSIS IN DIFFERENT SOILS

Clay A, St. Paul	0.0198
Dark gray clay, Pierre, South Dakota	0.0613
Yellow clay, Indiana	0.0915
Light gray clay, Havana, Cuba	0.0295
Yellow clay, Havana, Cuba	0.3240
Blue clay, Minneapolis	0.0597
Peat D, St. Paul	0.2300

Ingot iron, analysis 1, 1.3x2.5-in. polished plates. Grams iron lost after treating 528 hours in fibre cells. Water content approximately the natural percentage.

pressures within the range of pressures met in practice due to depths of burial.

Admitting or excluding air from a test cell has no appreciable effect on corrosion rates.

The life of underground iron structures could be greatly prolonged by placing a few inches of sand around them, especially in clay, cinders and moist electrolytically active soils.

Denver, Col.

## Distillation of Coal at Low Temperature\*

THE distillation of coal at a high temperature, such as is actually practiced in gas retorts to extract illuminating gas, takes place under unfavorable conditions from a thermal point of view. According to results obtained by M. Euchène, only 12 per cent of the heat produced by combustion is available for distillation. M. Guéguen, relying on the fact that transmission of heat through the retorts is slight and that this transmission decreases in proportion to the distillation, set about to determine whether it would not be profitable to induce distillation by the introduction of a current of steam superheated to from 500 to 700 deg. His investigations showed several advantages: Shorter distillation periods, distillation accomplished more quickly and more directly, easier liberation of the gas by entrainment and operation at lower temperatures.

In addition, it was of great interest to know whether the coal itself could serve as a raw material for the manufacture of the aromatic compounds as well as for that of the hydro-aromatic and aliphatic compounds, obtained up to the present time from coal tar.

Moreover, attempts have long been made to obtain a better utilization of the coal either by distillation in a vacuum or by distillation at low temperature. Up to now, distillation in a vacuum, studied especially by Berthelot and Pictet, has had no practical application.

In distilling coal under a pressure of 20 mm. of mercury at a maximum temperature of 450 deg., Pictet has obtained 4 per cent of liquid coal tar, containing neither naphthalene nor anthracene, both of which are characteristic of coke-oven tar; however, in heating this tar red hot in incandescent tubes, it is transformed into ordinary tar. Pictet states that the tar obtained in a vacuum contains a greater quantity of phenol than crude petroleum and does not polarize light.

The distillation of coal at low temperature, on the contrary, will perhaps find an immediate and practical realization, thanks to the investigations instituted for this purpose at the special institute for the study of coal created at Mulheim on the Ruhr. (See *Génie Civil*, March 10, 1917, p. 165.)

### INVESTIGATING MINERAL OILS

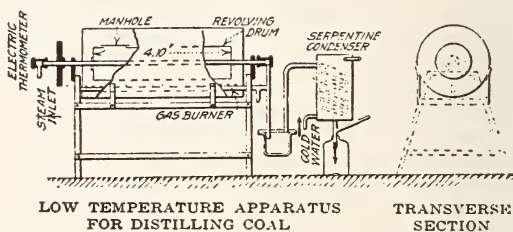
This Research Institute, created by the Kaiser Wilhelm Society to contribute to the development of theoretical and applied sciences has concerned itself particularly up to the

present time with practical questions of immediate interest, notably, the investigation of mineral oils. We know that since the war Germany has lacked oils of all kinds. Lubricating oils which are now used are for the most part mineral oils extracted from petroleum and imported largely from America. It would be very advantageous then for Germany to be able to extract the lubricants which she needs from the coal by distillation.

The investigation of new sources of volatile products, of lubricants or of motor oils has led this institute to undertake a minute study of the chemical nature of coal and also of coal distillation at low temperatures.

This question is not new; already in 1906 Börnstein, of Berlin, published (*Journal für Gasbeleuchtung*, Aug. 4, 1906) results of a systematic investigation made by him on the distillation of coal at atmospheric pressure and at a temperature no higher than 450 deg. The coke used was friable and porous, and useless in metallurgy. It yielded a brown tar in a proportion of 3 per cent for the rich coals and 10 per cent for the flaming coals and those not containing free carbon. These tars, studied by Börnstein, were in reality paraffines melting between 55 and 60 deg. and containing up to 28 per cent acid products; the oily elements of the tars, freed of basic and acid compounds, contained neither naphthalene nor anthracene.

Below 350 deg. it contained no solid bodies; above 350 deg. paraffines were obtained; the benzols did not contain thiophene. The quan-



tity of gas obtained was small, 17.6 liters of gas per kilogram of flaming coal from the Bismarck mine yielding 10 per cent tar.

In England some companies were formed for the distillation of coal at low temperature, among others the Coalite Company, which obtained in place of coke some coalite or semi-coke (See *Génie Civil*, March 14, 1918, No. 20, p. 348) which can be used as smokeless fuel, but the tar yield was very large and the coalites too friable.

\*Translated from *Le Génie Civil*, July 7, 1917.



## APPARATUS USED BY GERMAN INSTITUTE

In a conference on the actual state of the coal investigations held March 6 at the General Assembly of German Iron Masters and reproduced in Stahl and Eisen, April 12 and 19, Prof. Franz Fischer, director of the institute for the study of coal, discussed at great length the distillation of coal at low temperatures and described the apparatus used for this purpose by the German Institute.

This laboratory apparatus, represented in the illustration, is composed of an iron cylinder containing the combustible, heated by a gas flame and arranged to rotate slowly around on its axis (3.5 turns). With this arrangement, the particles of coal heated by direct contact with the walls cannot be overheated, for the layer in contact with the walls is constantly being replaced. Moreover, since the particles commencing to distil are brought back to the surface, the tar vapors do not encounter the layer of coal again, but are entrained and carried out of the drum by a current of steam introduced through the hollow shaft. An electric precision thermometer serves to show the temperature of the apparatus during the operation. The apparatus is completed by a deposit chamber and a coil immersed in water.

With this apparatus, complete distillation of coal is effected in one or two hours and there is obtained with rich coal 3 per cent tar, and with flaming coal 10 per cent tar, the composition of which is indicated in Table I.

TABLE I—COMPOSITION OF TARS EXTRACTED BY DISTILLATION OF COAL AT LOW TEMPERATURE

Composition, Per Cent	Tar from Rich Coal	Tar from Flaming Coal
Highly viscous oils (lubricants) ..	15.2	10.0
Paraffines.....	0.4	1.0
Non-viscous oils.....	33.5	15.0
Phenols.....	14.0	50.0
Resin.....	4.2	1.0
Residual tar.....	19.2	6.0
Losses and water.....	13.5	17.0
Total.....	100.0	100.0

M. Fischer says that by this method of distillation they obtained tars free from naphthalene and anthracene and containing paraffine. After the separation of the phenols, by distillation with superheated steam one can extract from the tar the lubricating oils forming 10 to 15 per cent of the weight of the coal and resembling those obtained in the treatment of coal by liquid  $\text{SO}_2$ . These lubricants, red-gold in color and possessing a pleasing odor, are mixtures of oil. They have been able to extract lubricating oils from them which ignite

at 200 deg. and have, at 50 deg. temperature, a viscosity of 2 deg. to 28 deg. (Engler). The oils set down in Table 1 as non-viscous are oils having the character of petrols and containing unsaturated hydrocarbons and true olefines of the formula  $\text{C}_n\text{H}_{2n}$ . They have been able to establish the fact that they polarize light weakly, which is quite characteristic of petrols.

## GASES OF HIGH CALORIFIC VALUE

The gases obtained during the distillation have a very high calorific value, about 9000 calories, and have a volume of 40 liters per kilogram of rich coal and of 50 liters per kilogram of flaming coal. This high calorific value is due to the presence of 70 per cent methane, ethane and heavy hydrocarbons.

They have not been able to separate the light hydrocarbons from the gases of distillation by the ordinary method; to accomplish this, they have had to distil the gases by steam after compression of 20 atmospheres in the presence of paraffine oil. They have thus obtained aromatic carbons in an amount of 0.2 to 0.3 per cent of the weight of coal boiling between 20 deg. and 100 deg. and containing almost no benzol. These hydrocarbons are a mixture of volatiles the specific gravity of which at 20 deg. is about 0.65. They yield different kinds of petroleum derivatives in distilling, such as petroleum ether, ligroin, light and heavy benzines. The tar still contains very nearly as much of these benzines, or a total of 0.3 to 0.6 per cent of the weight of coal.

These bodies, the exact chemical nature of which is not yet known but the analysis of which shows 83.5 per cent carbon and 14.5 per cent hydrogen, are more hydrogenated than benzol (7.5 per cent) and its homologs.

From the experiments made up to this time one can conclude that, if the distillation at low temperature is carefully conducted, it is possible to extract from the coal all the industrial products of petrol: paraffines, lubricants, benzines, oils.

The economic success of this distillation at low temperature depends particularly on the utilization of the coke produced. This should be obtained adequately solid; if not producers should be set up near the distilling apparatus, so that the coke can be used while still warm.

Already, thanks to the labors of Messrs. Parr and Olin at the University of Illinois, it has been possible to improve the quality of the coke obtained by mixing finely pulverized coal with the coke dust and compressing the briquet of coal during the distillation.



## Effect of Certain Accelerators Upon the Properties of Vulcanized Rubber

BY G. D. KRATZ AND A. H. FLOWER\*

THE relative accelerating effect of inorganic and organic accelerators has been subject to a diversity of opinion ever since the latter have been employed in technical practice. Likewise, the effect of each upon the quality and physical properties of the vulcanized rubber has been a matter of discussion.

The results recorded in the experimental part of this paper were obtained in the course of several investigations carried on for the joint purpose of determining the relative activity of certain inorganic and organic accelerators, and the permissibility in the use of the sulphur coefficient in evaluating samples of vulcanized rubber known to contain accelerators. As recorded here, this has consisted primarily in (a) a comparison of the relative effects of heavy calcined magnesia and an (unidentified) organic accelerator in a mixture containing only rubber and sulphur, and (b) a comparison of the effect of larger amounts of heavy calcined magnesia, light magnesia and lime in a mixture which contained an excess of zinc oxide.

Irrespective of the effect of accelerators upon the physical properties of the vulcanized mixture, possibly the advantage most often claimed for the organic variety in preference to inorganic substances is that, in accelerating vulcanization, the former are much more active than the latter and can be used in small amount to replace much larger quantities of litharge, magnesia or lime. Incidentally, the use of heavily pigmented mixtures is avoided by this substitution. Van Huern<sup>1</sup> and many others<sup>2</sup> have given figures subject to this interpretation. In a recent communication, however, H. P. Stevens<sup>3</sup> has taken exception to this view, and, further, has obtained results which show that magnesia is more powerful than the inorganic accelerator litharge, or even the organic accelerator isonitroso-dimethyl-aniline. While Van Heurn has also given figures for vulcanization coefficients which show that magnesia is more powerful than litharge, unlike Stevens, he found one-fourth of 1 per cent of p-nitroso-dimethyl-aniline to be more active than even 1 per cent of magnesia.

### GENERAL PART

Although our investigations have not in-

cluded a comparison of the relative effects of magnesia and p-nitroso-dimethyl-aniline, the organic accelerator which we employed in place of the latter substance was found to be far more active, when used in small amounts, than were similar quantities of magnesia. Likewise, the physical properties of the mixtures which contained the organic accelerator were shown to be superior to those obtained with similar amounts of magnesia. This, however, did not at first appear to be the case owing to discrepancies found to exist when the load required to effect a given extension is taken as a measure of the physical properties<sup>4</sup>. In this instance then, the sulphur coefficient may be said to afford a fair index of the state of cure, as measured by the physical properties, of mixtures known to contain small amounts of either inorganic or organic accelerators.

This statement, however, was not found to be of general application, and certainly is not true for mixtures which contain larger amounts of inorganic accelerators in the presence of an excess of zinc oxide. We have never regarded zinc oxide itself in the same manner as Van Heurn<sup>5</sup>, who found it to act as a retardant of the vulcanization reaction. Nor have we, with King<sup>6</sup>, classed it, strictly speaking, as an accelerator. Our experience has been more similar to that of Ditmar and Theiben<sup>7</sup>, who found that large amounts of zinc oxide effected a slight, and limited, increase in the rate of vulcanization (sulphur coefficient).

On the other hand, contrary to what might be expected, we have found that mixtures which contained fairly large quantities of both magnesia and zinc oxide, when vulcanized to maximum physical properties, had lower sulphur coefficients than a control mixture which was vulcanized to the same degree without the assistance of an accelerator. The substitution of lime for magnesia in such a mixture, however, was found to produce quite a different effect. With lime, after an initial decrease in the sulphur coefficient, the latter value was found to respond to a further increase in the amount of accelerator. This difference in the action of the two substances would indicate that their function in the mixture is not identical.

Our results with heavy mineralized mix-

\*Read before the New Jersey Chemical Society, Jan. 13, 1919.

tures have shown that such mixtures are not only subject to misinterpretation, but also that (as has already been stated by Eaton and Grantham<sup>8</sup>) the constituents of the mixtures tend to obscure or mask the individual properties of the rubber used. With this the case any formula, such as proposed by Dannerth and Gage<sup>9</sup>, is untenable for the valuation of raw rubbers.

Fundamentally, the purpose of any ordinary vulcanization is to obtain the maximum physical properties which the mixture will retain unimpaired over the longest period of time under the conditions to which it will be subjected. Our experience in the past has been that this physical condition may be largely independent of the sulphur coefficient, particularly if the mixture has been vulcanized with the assistance of an accelerator. Generally speaking, we have not found that the sulphur coefficient affords a reliable indication of the physical properties of a vulcanized rubber mixture or that it can be taken as a measure of the state of cure except possibly in the case of mixtures which consist of rubber and sulphur only. We agree with Stevens<sup>10</sup>, however, that for *hevea* rubber practically all mixtures with a sulphur coefficient in excess of 3.2 will be subjected to rapid deterioration.

In a former paper<sup>11</sup> we have given the limits for the vulcanization coefficient of *hevea* rubber at 1.7 to 2.8. Under standardized conditions, the higher figure has been found to be constantly approximated by mixtures vulcanized without the aid of an added accelerator, or with the assistance of one which is only mildly active. The lower figure has been found to apply for mixtures vulcanized with the assistance of even small amounts of powerful organic accelerators or larger amounts of magnesia. The anomaly found to exist between the action of magnesia and lime, however, indicates that a certain amount of reservation should be made in interpreting the coefficients of mixtures which contain either of these substances.

In view of our results as a whole, while we agree with Stevens<sup>12</sup> that the sulphur coefficient is most important as an indication of the ultimate stability of the product, in general practice it should be considered as an indication only. Even in the case of mixtures composed solely of rubber and sulphur we have found it dangerous to evaluate between them on the strength of their sulphur coefficients alone, unless the past histories of the samples in question are definitely known. As Stevens<sup>13</sup> has stated in a subsequent communication, the true value of a product, as expressed by its state of cure, is obtained from physical and chemical tests only when they have been made after a definite period of aging conducted un-

der carefully standardized conditions. Our results along these lines will be reported upon in the near future.

#### EXPERIMENTAL PART

As a considerable portion of the work described in this part was carried on prior to our repetition of Stevens' experiments, the same sample of rubber could not be used throughout. However, the same sample of rubber was employed for all the mixtures in each of our experiments.

The rubber used was good quality, thin pale first latex (*hevea*) crêpe. In each instance the sample was subjected to the minimum amount of milling necessary to work in all of the ingredients. Where small quantities of accelerators were used the total time of each mixture on the mill was 18 to 20 minutes<sup>14</sup>; with the mixtures which contained larger amounts of accelerators and zinc oxide this time was increased to 22 to 25 minutes. All mineral substances were previously sieved through a 100-mesh screen.

The heavy calcined magnesia was previously ignited and found to contain 92.73 per cent MgO. Specific gravity 3.24.

The extra light magnesia gave a loss of 4.0 per cent on ignition, after which it was found to contain 94.0 per cent MgO. Specific gravity 2.82.

The lime was air slaked, gave a loss on ignition of 13.46 per cent and contained 55.12 per cent Ca(OH)<sub>2</sub>. Specific gravity 2.19.

The zinc oxide was lead free. Specific gravity 5.64.

Accelerator "A" was prepared by the condensation of an amine with formaldehyde. It was of C. P. quality.

In all instances, after mixing, a rest period of 24 hours was allowed before vulcanization. A recovery period of 7 days was then permitted before physical tests or sulphur estimations were made. The combined sulphur was estimated by the method of Rosenstein-Davies<sup>15</sup>: the samples, having first been subjected to 24 hours continuous extraction with acetone in a Soxhlet apparatus, were dried in air and then in vacuo at 100 deg. C. to constant weight. The sulphur coefficients given represent the combined sulphur of vulcanization expressed as a percentage of the rubber in the mixture.

$$\text{Sulphur coefficient} = \frac{\text{per cent combined sulphur in the mixture}}{\text{per cent rubber in the mixture}}$$

The physical properties of the mixtures which contained small amounts (0.10 to 1.25 per cent) of accelerators were measured by the method employed by Stevens, *i.e.*, measurement of the load required to effect an ex-



tension of one to nine, and also at break for tensile strength and percentage elongation. In making this comparison, figures for both methods were obtained on the same sample or test piece by recording the load required to effect the given extension and then increasing the load and continuing the extension to breaking point. Each figure given in the following tables is the average of at least three test pieces.

Irrespective of the adaptability of the two methods as a means of testing samples of different mixtures, both of them are subject to criticism. The measurement of the load required to effect an extension of one to nine was unsatisfactory in that even small amounts of magnesia decreased the percentage elongation to such an extent that this extension was made just short of the point of rupture, or break. The danger of misinterpreting the results obtained by this method, due to this feature, is commented upon elsewhere in this article. This method would be more generally applicable if the load required to effect a lesser extension was recorded. On the other hand, when tested at break, the samples which contained but small amounts of accelerators had a tendency to be cut by the clamp holding the test piece, before the point of rupture was reached.

NOTE: The mixtures which contained zinc oxide were tested at break only. All results were obtained on a Scott testing machine of the vertical type.

#### EXPERIMENT 1

In this experiment we first followed the plan outlined by Stevens and have compared the accelerating effect of magnesia against an organic accelerator which we have called Accelerator "A." The effect of these accelerators was tested in the same mixture as previously employed by Stevens, namely, 90 parts of rubber and 10 parts of sulphur<sup>16</sup>, with added amounts of the accelerators varying from 0.10 to 1.25 per cent on the rubber content. Vulcanization was carried on in a platen press for 60 minutes at 35 lb. steam pressure (281 deg. F.), after which sulphur estimations and measurements of the physical properties were made on the vulcanized products in the manner previously described.

We found the vulcanization coefficients of the series actuated by our "Organic Accelerator A" to be uniformly higher than those obtained with similar amounts of magnesia. (Col. 3, Tab. I, and Fig. 1). This difference between the results obtained by Stevens and us is readily accounted for in the selection of the organic accelerators employed. His accelerator, as well as our own, is unidentified. When the physical properties of our two series

of mixtures were expressed in the manner adopted by Stevens, that is, by the measurement of the load required to effect an extension of 1 to 9, Accelerator "A" was found to have a slight advantage up to about 0.5 per cent, at which point magnesia produced superior results. (Col. 4, Tab. I, and Fig. 1A.) Thus, the physical properties of the series which contained Accelerator "A" are seen to be at variance with what would be expected from their respective sulphur coefficients, provided that the latter figures can be taken as

TABLE I

Accelerator used	Per Cent Accelerator	Sulphur Co-efficient	Load in G. per Sq. Mm. Extended 1 to 9	Tensile Strength in G. per Sq. Mm. (at Break)	Per Cent Elongation at Break
Heavy Calcined Magnesia	0.00	0.684	163	181	962
	0.10	1.012	...	564	937
	0.25	1.287	501	774	950
	0.50	1.500	633	766	912
	0.75	1.873	832	914	900
Accelerator "A"	1.00	1.724	886	914	912
	1.25	1.821	883	1002	918
Accelerator "A"	0.00	0.684	163	'8	962
	0.10	1.202	402	621	925
	0.25	1.609	630	871*	900*
	0.50	2.079	678	1153*	975*
	0.75	2.347	664	1170*	1025*
Accelerator "A"	1.00	2.518	636	1250*	1037*
	1.25	3.004	642	1223	1087

\*These samples were pinched through by the clamps of the testing machine before the point of rupture, or break, was reached. Consequently, the results for tensile strength and elongation at break are low.

TABLE II.

Accelerator Used	Mixture	Per Cent	Per Cent	Per Cent	Per Cent
Heavy Calcined Magnesia	First Latex.....	100	100	100	100
	Zinc Oxide.....	100	92	83	74
	H. C. Magnesia...	...	5	10	15
	Sulphur.....	5	5	5	5
Light Magnesia...	First Latex.....	...	100	100	100
	Zinc Oxide.....	...	90	80	70
	Light Magnesia...	...	5	10	15
	Sulphur.....	...	5	5	5
Lime.....	First Latex.....	...	100	100	100
	Zinc Oxide.....	...	87	75	62
	Lime.....	...	5	10	15
	Sulphur.....	...	5	5	5

TABLE III.

Accelerator Used	Per Cent Accelerator	Time in Minutes for Technical Cure at 298° F.	Tensile Strength at Break, G. per Sq. Mm.	Elongation at Break, Per Cent	Sulphur Coefficient
Control .....	0	120	1,331	725	3.075
Heavy Calcined Magnesia	5	90	1,553	700	2.586
	10	75	1,627	725	1.723
	15	45	1,402	675	.....
Light Magnesia...	5	90	1,322	700	2.780
	10	45	1,875	750	2.184
	15	40	1,350	775	.....
Lime.....	5	90	1,294	800	1.909
	10	45	1,565	750	2.926
	15	40	1,512	750	.....

an indication of the state of cure, as measured by the physical properties.

As the series which contained Accelerator "A" appeared to be much superior to the corresponding mixtures containing magnesia, when judged by the "thumb and tooth," it was felt that the physical properties of the two series were not fully expressed by the above method. They were then expressed in terms of the tensile strength and percentage elongation at break.

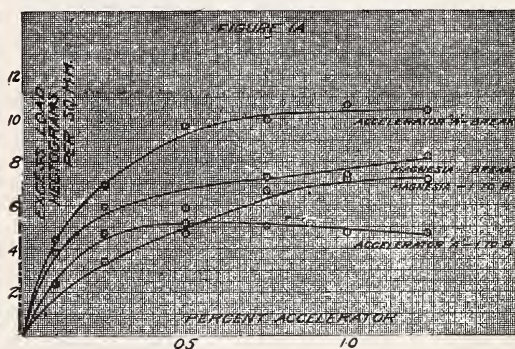
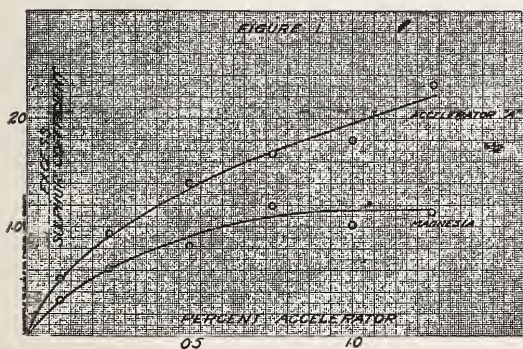
When interpreted in light of these results (Cols. 5 and 6, Table I, Fig. 1A), an entirely different relation was seen to exist. Even in this instance, however, it cannot be said that a direct relationship exists between the sulphur coefficients and physical properties of the various mixtures. In the cases of the mixtures vulcanized with the assistance of Accelerator "A," it is evident from the figures obtained for the percentage elongation at break that this property increased coincidentally with an increase in the tensile strength<sup>17</sup>; with magnesia, on the contrary, the tensile strength was increased at the expense of the elongation.

This difference in the effect produced in the percentage elongation by small amounts of accelerators prohibits the use of the load required to effect a given extension as a measure of the physical properties of the two series of mixtures. As the percentage elongation of a

with 1 per cent of this substance, an extension of one to nine was produced only by a load just short of that required to produce rupture, or break.

#### EXPERIMENT 2

In the following work, where much larger amounts of inorganic accelerators were employed, it was desired that the effect of the accelerator as a filler should be minimized to the greatest possible extent. This was accomplished by employing mixtures which contained zinc oxide in such an excess that from 5 to 15 per cent of an inorganic accelerator could be included in the mixture, by replacement of a similar volume of zinc oxide, without decreasing the effect, or function, of the latter substance (Tab. II). The sulphur content of the various mixtures was also cut down from 11 to 5 per cent, calculated upon the rubber. In this instance, and unlike the preceding experiments, the mixtures were vulcanized to maximum physical properties and their respective sulphur coefficients determined at this point. Portions of each of the mixtures were vulcanized in a platen press at 50 lb. steam pressure (298 deg. F.) over a wide range of times and the correct cure determined as the point of coincident, maximum tensile strength and percentage elongation (technical cure<sup>18</sup>). The sulphur coefficient of each mixture when vulcanized to this degree was then determined (Col. 6, Tab. III).



mixture is increased, by the action of an organic accelerator or otherwise, unless this is accompanied by a corresponding and uniform increase in the tensile strength, a given extension will be effected by a lesser load than would normally be required. This was roughly found to be true with Accelerator "A." On the other hand, when tensile strength is increased at the expense of the elongation, as was found to be the case with magnesia, it will require an excessive load to effect the same extension. This decrease in the percentage elongation of mixtures which contained small amounts of magnesia was so marked that,

The results obtained show that, for all three of the accelerators used, the best physical properties were obtained with about 10 per cent of each in the mixture. The effects produced by light magnesia, heavy calcined magnesia and lime ranked in the order named. These differences, however, were small enough to be accounted for in the value of each of these substances as a filling material. However, it is evident that the value of these accelerators as filling materials is of limited extent, because, when present in larger amount (15 per cent), in each case the vulcanized mixtures showed inferior physical properties



(Cols. 4 and 5, Tab. III). Moreover, the sulphur coefficients of the various mixtures were not found to reflect, or be a measure of, their physical properties. With both varieties of magnesia, the mixtures which contained 10 per cent of these substances were found to have lower sulphur coefficients than the mixtures which contained but 5 per cent, and the latter had lower coefficients than the control which was vulcanized without the assistance of an accelerator. On the other hand, the results obtained with lime were remarkable in that with 5 per cent of this substance, a much lower sulphur coefficient was obtained than in the case of the control, while with 10 per cent, contrary to the results obtained with magnesia, the sulphur coefficient was increased almost to that of the control.

In explanation of the results obtained with magnesia, we have consistently found that mixtures vulcanized quickly to maximum physical properties with the assistance of accelerators invariably show lower sulphur coefficients than similar mixtures also vulcanized to maximum physical properties but without the assistance of an accelerator. Frequently, much higher physical values are developed by those mixtures which contain accelerators. The same is true in lesser extent when a short period of vulcanization is effected by the use of higher temperatures. It is at least indicated that the time required to effect the cure of a given mixture is reflected both in its sulphur coefficient and physical properties.

#### CONCLUSIONS

In view of the foregoing results we have been led to the following:

1. That the physical properties of vulcanized rubber mixtures are more fully expressed in terms of the tensile strength and elongation at break than by the load required to effect an extension of one to nine.

2. When used in small amount magnesia is less active in accelerating vulcanization than certain organic accelerators, and it does not impart to the mixtures the physical improvement characteristic of the latter substances.

3. With mixtures which contain even small amounts of either inorganic or organic accelerators, no direct relationship exists between the sulphur coefficient and the state of cure as measured by the physical properties of the mixture.

4. When mixtures are vulcanized quickly with the assistance of inorganic accelerators, the correct state of cure, as reflected by their physical properties, is obtained at abnormally low sulphur coefficients.

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<sup>1</sup>Intern. Assoc. Rubber Cult. in Netherland Indies. Comm. of Netherland Govt. Inst. for Advising Rubber Ind., Part VI, p. 202.

<sup>2</sup>D. R. P. No. 265,221 (1912). D. R. P. No. 269,512 (1913). Brit. Pat. No. 4263 (1914). *Gummi. Ztg.*, 30, (1916), 303, 326.

<sup>3</sup>*India Rubber J.*, 55, (1918), 25, 5.

<sup>4</sup>This method as employed by H. P. Stevens [*India Rubber J.*, 55, (1918), 25, 5] and others, was found to be subject to correction, as it assumes that, in making comparisons between several samples, similar extensions will be effected by similar loads. Beadle and Stevens [*J. Soc. Chem. Ind.*, 30, (1911), 1421] have previously shown that the addition of as little as one-half of 1 per cent of zinc oxide or talc will produce a marked decrease in the extension of the vulcanized mixture. We have found the same to be true for small amounts of magnesia: certain organic accelerators, however, were found to increase the extension. With such the case, entirely erroneous results were obtained when two series of mixtures, one of which contained small amounts of magnesia and the other similar amounts of a strong organic accelerator, were tested by this method. We have found that comparisons made on the basis of the loads required to effect a given extension are less reliable than those obtained by comparing the tensile strength and percentage elongation at break.

<sup>5</sup>Intern. Assoc. Rubber Cult. in Netherland Indies. Comm. of Netherland Govt. Inst. for Advising Rubber Ind., Part VI, p. 202.

<sup>6</sup>*MET & CHEM. ENG.*, 15, (1916), pp. 231-4.

<sup>7</sup>*Kolloid Z.*, 11, (1912), pp. 77-80. In the course of this work, Ditmar and Thieben also found that lime under vulcanizing conditions showed a greater tendency to form thin compounds than other substances such as MgO, ZnO, etc. In view of this, and the results obtained in experiment 2, we are led to class the action of lime in accelerating vulcanization as more similar to that of litharge than to that of magnesia.

<sup>8</sup>*J. Soc. Chem. Ind.*, 35, (1916), pp. 1046-50.

<sup>9</sup>*India Rubber World*, 56, (1917), pp. 533.

<sup>10</sup>*India Rubber J.*, 56, (1918), p. 2.

<sup>11</sup>*J. Ind. Eng. Chem.*, 11, (1919) p. 30.

<sup>12</sup>*India Rubber J.*, 53, (1917), p. 220.

<sup>13</sup>*J. Soc. Chem. Ind.*, 37, (1918), p. 280.

<sup>14</sup>Where less than 1 per cent of a mineral accelerator is worked into a rubber, it is extremely doubtful that it becomes uniformly distributed throughout the mass. When used in small amount (up to 3 per cent), and compared on the basis of their respective lead contents, we have found lead oleate to be more active in accelerating vulcanization than litharge. We attribute this largely to the unctuous nature of the lead oleate, which lends itself to a better incorporation with the rubber than litharge.

<sup>15</sup>*Chemist Analyst*, 15, (1916).

<sup>16</sup>The use of such a large quantity of sulphur is deprecated on the ground that it is in excess of the amount required to give a good vulcanization, particularly when employed in a mixture which also contains an accelerator. The excess of sulphur undoubtedly acts as a "filler," the effect of which is commented upon later in this experiment.

<sup>17</sup>Van Rossem (Reference No. 1, p. 214) has already noted that rubbers vulcanized with the assistance of certain organic accelerators show an increase in their percentage elongation at break. In this connection he has also found that, with similar amounts of an accelerator, the vulcanization of a rubber with a low viscosity value will be accelerated more than a rubber with a high viscosity value. This is explainable in light of the results of Spence and Kratz [*Kolloid Z.*, 14 (1914), p. 265], who found that small traces or acid decreased the viscosity of a rubber solution. As Van Heurn (*loc. cit.*) and others have found practically all accelerators of vulcanization to be basic, and retardants to be acidic, the accelerator is doubly effective in the case of rubbers of low viscosity in that it first counteracts the effect of the retarding agent and then accelerates the vulcanization. This will also account for the greater uniformity which is obtained in the rate of vulcanization of rubbers of widely different viscosity values when vulcanized with the assistance of an accelerator.

<sup>18</sup>*J. Ind. Chem. Eng.*, 11, (1919), p. 30.

## A Study of the Lime-Soda Ash Water-Softening Process

BY MAX R. HERRLE AND FRANCIS M. GLEESON

**I**N THIS article it is our desire to call particular attention to that branch of factory control relating to the filtering, softening and purifying of water. It is an accepted fact among power plant engineers and users in general that pure clear water is essential for industrial as well as domestic use, and especially that soft clear water for boilers is a great factor in expense saving by reducing fuel bills, repairs and labor incidental to keeping boilers and heaters clean and in first class working condition.

All water on this earth has descended from the clouds at one time or another. This water in its descent has absorbed carbonic acid, air and many other impurities. The carbonic acid absorbed enables the water to dissolve many salts, chief among them being those of lime and magnesium. The common impurities are:

1. Carbonates of lime, magnesium, sodium and potassium.
2. Sulphates of lime, magnesium, sodium and potassium.
3. Nitrates of lime, magnesium, sodium and potassium.
4. Chlorides of lime, magnesium, sodium and potassium.
5. Silica and the oxides of iron and aluminum.
6. Suspended matter, as sand and mud.
7. Organic matter.
8. Carbonic acid.

These impurities are common to all waters to a greater or less extent, and it is their removal that has been the subject of many discussions and writings. There are several methods that are adaptable for the removal of these soluble impurities, and a discussion of their adaptability and practicability will now follow.

### THREE CLASSES OF WATER PURIFICATION

In a general sense the subject of water purification may be divided into three classes: Distillation, filtration, and chemical purification by precipitation.

Distillation, although ideal, is too expensive to be considered for supplying large quantities of water.

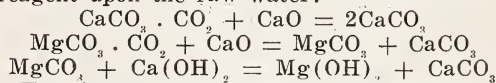
Filtration is of value only when a soft dirty water is to be had, as the dirt will be

removed in the process, but should the water be hard due to the presence of soluble impurities, as is the case with most waters, filtration will be of value only after the soluble salts have been converted into the insoluble state.

Therefore, the only method remaining to purify a water for boiler use is chemical purification by precipitation. This method is the one that is used almost universally and the one that will give the best results under the most adverse conditions.

Having discussed the natural substances whose presence in the water supply is detrimental to steam boilers and in other industrial processes, the first thought which naturally occurs in studying the question is the use of some reagent or process which will effectively precipitate the scale-forming material so that the same may be readily removed before the water is used. The complete softening of a water requires the removal both of its temporary and of its permanent hardness. The temporary hardness of a water is caused by the carbonates of lime and magnesium being held in solution by an excess of carbonic acid. These carbonates, which are practically insoluble in pure water, can be precipitated by removing the carbonic acid. This removal is accomplished by means of lime.

This lime is added as a solution and the following equations illustrate the effect of this reagent upon the raw water:



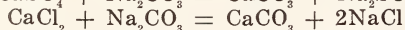
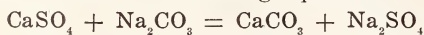
The lime unites with the acid carbonate of calcium to form the insoluble calcium carbonate, which then precipitates out. It also combines with the acid carbonate of magnesium to produce the insoluble carbonate of magnesium, which is further converted into the more insoluble magnesium hydrate and in turn precipitates out. The lime further effects a practically complete precipitation of the remaining magnesium compounds.

Thus we see that by the addition of lime as a reagent we secure a precipitation of the calcium and a practically complete removal of all the magnesium compounds because of the fact that the lime removes the carbonic acid which holds the hardness-forming salts in solution.

Permanent hardness of raw water is caused by the sulphates, chlorides and nitrates of calcium and magnesium. Since magnesium compounds have been removed, the remaining



permanent hardness of the water is eliminated by means of sodium carbonate, which precipitates the insoluble calcium compounds in accordance with the following equations:



The sodium carbonate unites with the calcium sulphate to give the insoluble calcium carbonate, which precipitates out. The sodium carbonate further unites with the calcium chloride to give the insoluble calcium carbonate.

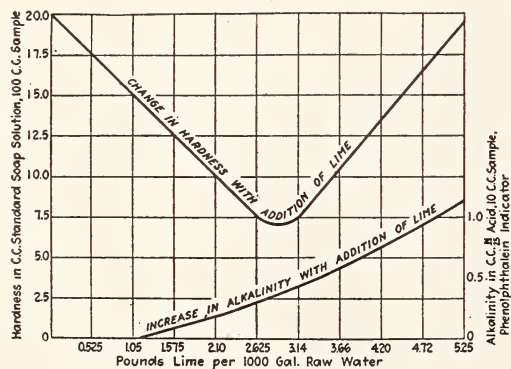
Thus we see that after the addition of the sodium carbonate all the hardness and scale-forming salts have been removed and only neutral and non-corrosive substances are left in solution.

It is now evident that by means of the two reagents, lime and soda ash, an ideal water can be secured with but one problem to face us, that in order to secure this water having a relatively low hardness and alkalinity great care must be taken in adding the reagents. We have carried out a series of tests which we hope will aid in effecting a correct proportioning of the reagents. They are as follows:

*Test I.* This test deals with the addition of lime to raw water and shows the effect of an insufficient amount of lime, the effect of the correct amount and the effect of an excess.

*Test II.* This test deals with the addition of soda ash to a raw water and illustrates the effect of an insufficient addition, a correct addition and the effect of an excess.

*Test III.* This test deals with the addition of both reagents to raw water and shows the



CHANGE OF HARDNESS AND ALKALINITY WITH ADDITION OF LIME

correct adjustment of reagents which is absolutely necessary for the production of a good boiler feed water.

Following the tests there is a paragraph dealing with the value of water analysis which also contains the analysis of our raw and treated waters.

#### TEST I. EFFECT OF LIME (CAO) UPON RAW WATER

A 30-gal. sample of raw water was taken for this experiment. The water had a hardness of 20.0 deg. with standard soap solution and no alkalinity with N/25 acid, using phenolphthalein as an indicator. The water was treated with successive charges of hydrated lime, which was added as a solution by mixing each charge with some of the water of the original sample. After each addition the entire sample was very thoroughly stirred so as to insure a complete and uniform precipitation. The hardness and alkalinity were then tested for as above.

Turning our attention to the graph, it will be noticed that the hardness of the water decreased uniformly after each charge until the hardness of 7.0 deg. was reached, which is the minimum that can be obtained with lime alone. Upon further charging, the hardness increases uniformly but much more rapidly.

The hardness curve may be explained as follows: The hardness decreases uniformly as long as the chemical action between the lime and raw water takes place. When this chemical action is complete the water is at its minimum hardness and any further addition of the lime tends only to introduce an excess of this reagent and increase the hardness and alkalinity of the water.

This conclusion is substantiated when an examination of the alkalinity curve is made. No alkalinity is observed until the second charge, after which the alkalinity rises uniformly until the minimum hardness is reached, then the alkalinity increases at a greater rate, owing to the excess free lime.

The results of this test were calculated to pounds of lime per 1000 gal. of raw water to make them of more value to the engineer. Table I will show the amount and the effect of each addition.

TABLE I.  
EFFECT OF LIME (CAO) UPON RAW WATER

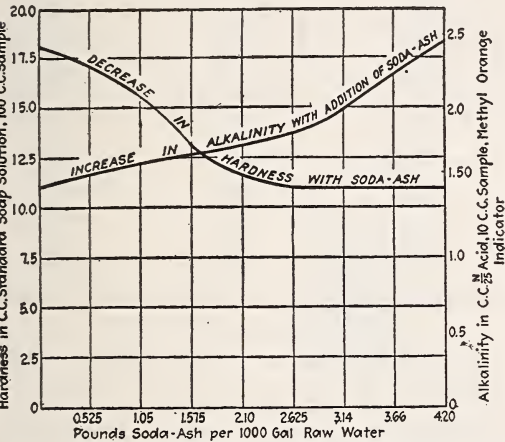
Lb. Lime per 1000 Gal. Raw Water	Hardness in c.c. Standard Soap Solution	Alkalinity in c.c. N/25 Acid Phenolphthalein as Indicator
0 0	20.0	None
0 52	17.5	None
1 05	15.0	None
1 57	12.5	0.08
2 10	10.0	0.20
2 62	7.5	0.30
2 91	7.0	0.36
3 14	7.5	0.43
3 66	10.5	0.53
4 20	13.5	0.75
4 72	16.0	0.93
5 25	19.5	1.13

The results of this experiment may be summarized as follows: Sufficient lime should be added to cause the chemical action between

the lime and raw water to go to completion, but an excess of this reagent is to be avoided, as it will increase the hardness and alkalinity very noticeably.

TEST II. EFFECT OF SODA ASH ( $\text{Na}_2\text{CO}_3$ ) UPON RAW WATER

A second experimental run was made with 30 gal. of raw water, using successive charges of soda ash. The soda ash was added as a solution by mixing each charge with some of the water of the original sample. After each addition the sample was mixed and tested for



CHANGE OF HARDNESS AND ALKALINITY WITH ADDITION OF SODA ASH

hardness and alkalinity, as in the lime experiment, excepting that methyl orange was used as the indicator.

Turning our attention to the accompanying graph, it will be seen that the hardness decreases rapidly after each successive charge until the minimum of 11.0 deg. is reached. This is the minimum that can be obtained with the use of soda ash alone, and marks the point at which the chemical action between the soda ash and raw water is complete. Further addition of soda ash produces no change, serving only to introduce an excess of the reagent and consequently increasing the alkalinity. An excess of soda ash is not to be feared, as apparently it has no effect on the hardness of the water, although it does increase the alkalinity.

Turning our attention to the alkalinity curve, we see that the alkalinity increases uniformly until the minimum hardness has been reached, after which the sudden upward trend of the curve tells us that excess of the reagent has been introduced and that no more soda ash need be added.

The results of this test were then calculated to pounds of lime per 1000 gal. of raw water in order to make them more convenient for the

TABLE II. EFFECT OF SODA ASH ( $\text{Na}_2\text{CO}_3$ ) UPON RAW WATER

Lb. Soda Ash per 1000 Gal. Raw Water	Hardness in c.c. Standard Soap Solution	Alkalinity in c.c. N/25 Acid Methyl Organe as Indicator
0.0	18.0	1.45
0.52	16.0	1.55
1.05	15.5	1.65
1.57	13.0	1.70
2.10	11.5	1.75
2.62	11.0	1.85
3.14	11.0	2.00
3.66	11.0	2.25
4.20	11.0	2.43

engineer to follow. Table II shows the amount and the effect of each addition of the reagent.

The results of this experiment may be summarized as follows: Sufficient soda ash should be added so that a slight excess of this reagent remains after the chemical action between it and the water has been completed. The excess will have no effect upon the hardness and but little effect on the alkalinity, so that the engineer need have no fear of its presence. This excess will prove of great value in case the raw water varies in initial hardness, as such small fluctuations can be readily cared for by this reagent.

TEST III. EFFECT OF LIME AND SODA ASH UPON RAW WATER

We have heretofore discussed the effect produced by the addition of lime and soda ash with regard to each curve separately, and now we will discuss the effect of the addition of both soda ash and lime together upon a sample of raw water.

We have found that the addition of lime to raw water produces a minimum hardness of 7.0 deg. by precipitating the soluble hardness-forming salts of magnesium and lime, but other salts of these elements still remain in solution and cannot be removed by lime but will be removed by soda ash.

Now the addition of soda ash to raw water produces a minimum hardness of 11.0 deg. by removing to some extent the hardness-forming salts of lime and magnesium, but other salts of these elements still remain in solution and cannot be removed by soda ash, but will be removed by the addition of lime.

Now it is obvious that by adding both reagents in their proper proportions, theoretically all the hardness-forming salts would be removed and an ideal water result. This is the experiment which will now be carried out to test the value of the theory.

A 30-gal. sample of raw water was obtained as in the preceding experiments and treated with sufficient lime to produce the lowest possible hardness obtainable with lime alone. This datum was obtained from the lime-water graph. Lime was added first instead of soda



ash because an added excess of lime will be cared for by the addition of soda ash later on. The mixture was thoroughly stirred and allowed to set for some time. Upon testing we found that the water had dropped from a hardness of 20.0 deg. to one of 7.0 deg. Now successive charges of soda ash were added, as in the soda ash experiment, and the mixture thoroughly stirred after each addition and a sample taken to be tested as in the previous tests.

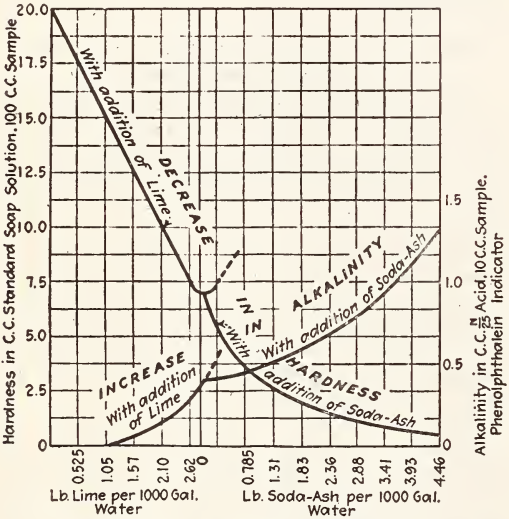
Turning our attention to the hardness curve, we find that the hardness decreases rapidly with the successive charges until the minimum of 0.5 deg. is reached, after which no further decrease is obtainable. The theoretical hardness of 0.0 deg. is not obtainable, being probably due to the small sample of water originally treated. In the water-softening system in operation at our plant it is nothing unusual to obtain a hardness of 0.0 degree.

Turning our attention to the alkalinity curve, we find that the addition of soda ash retarded the upward trend of the alkalinity, as indicated by the dotted line, and caused it to rise more slowly until at the minimum hard-

The same is true of the alkalinity curve. Upon the addition of lime the curve takes a rapid upward trend until the addition of soda ash, when its upward trend is decidedly retarded and a more gradual rise takes place. Table III shows the amount and effect of each addition of lime and soda ash upon raw water.

TABLE III. SHOWING QUANTITIES OF LIME AND SODA ASH IN COMBINATION CURVE

Charge in Lb. per 1000 Gal.	Hardness in c.c. Standard Soap Solution	Alkalinity in c.c. N/25 Acid
LIME		
0.00	20.00	0.00
0.525	17.50	0.00
1.05	15.00	0.00
1.57	12.50	0.066
2.10	10.00	0.13
2.63	7.50	0.25
2.93	7.00	0.40
SODA ASH		
0.00	7.00	0.40
0.26	5.25	0.41
0.0785	3.00	0.43
1.31	2.50	0.50
1.83	2.00	0.58
2.36	1.50	0.66
2.88	1.00	0.76
3.41	0.75	0.92
3.93	0.65	1.09
4.46	0.50	1.30



CHANGE WITH CONSECUTIVE ADDITIONS OF LIME AND SODA ASH

ness the alkalinity is 1.3 degree. This action of the soda ash upon the lime-treated water is very well illustrated in the combination curves which are graphically presented. For instance, an examination of the hardness shows the downward trend of the curve until the minimum hardness due to lime alone has been reached; the dotted curve shows the results of further addition of this reagent. The soda ash begins where the lime has left off and takes the hardness down to its minimum of 0.5 degree.

THE ANALYSIS OF WATER

As before stated, all water contains soluble impurities to some extent, and, since the removal of these salts is the chief question in the production of boiler-feed water, knowledge of which salts and the quantity of each is of the greatest importance in determining the amount of precipitating reagents to be used. This knowledge is secured from the analysis of the raw water. By this means the amount of precipitant can be regulated with accuracy.

The table below gives a complete analysis of the water with a hardness of 20.00 before treatment, and of the same water with a hardness of 0.50 obtained in the combination lime and soda ash experiment. The analysis as outlined in Stillman's Engineering Chemistry was followed. The quantities of salts are figured in grains per U. S. gallon.

	Raw Water	Treated Water
Hardness.....	20.00	0.50
Alkalinity with phenolphthalein....	None	1.30
Silica.....	0.35	0.35
Oxides of iron and alumina.....	Trace	Trace
Calcium carbonate.....	10.04	1.52
Magnesium carbonate.....	5.70	None
Sodium carbonate.....	None	0.23
Calcium sulphate.....	2.72	None
Sodium sulphate.....	None	3.89
Magnesium Chloride.....	0.42	None
Magnesium hydrate.....	None	0.39
Sodium chloride.....	1.87	1.58
Sodium hydrate.....	None	0.82
Volatile and organic matter.....	0.60	0.15
Total solids.....	21.41	8.93

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## The Manufacture of Hydrocyanic Acid

BY H. A. PELTON AND M. W. SCHWARTZ\*

**H**YDROCYANIC acid was produced for use in the manufacture of cyanogen chloride and for other experimental work. The problem of hydrocyanic acid manufacture may be of interest commercially in connection with the fumigation of fruit trees. At the present time most of the hydrogen cyanide employed for this purpose is prepared on the grounds from cyanide and sulphuric acid, inclosing the trees to be treated in a tent. By employing liquid hydrocyanic acid in cylinders, the trees can be treated with an attendant

phuric acid; the water vapor in the evolved gases is removed by fractional condensation, and the concentrated hydrogen cyanide is then condensed at atmospheric pressure. To expel hydrogen cyanide dissolved in the reaction mixture, the latter must finally be brought to the boiling point. Hydrocyanic acid forms dark tars with excess of sodium cyanide, and the cyanide is therefore added to the acid and an excess of the latter over the theoretical amount is employed. The residual liquor in the apparatus after the completion of the re-

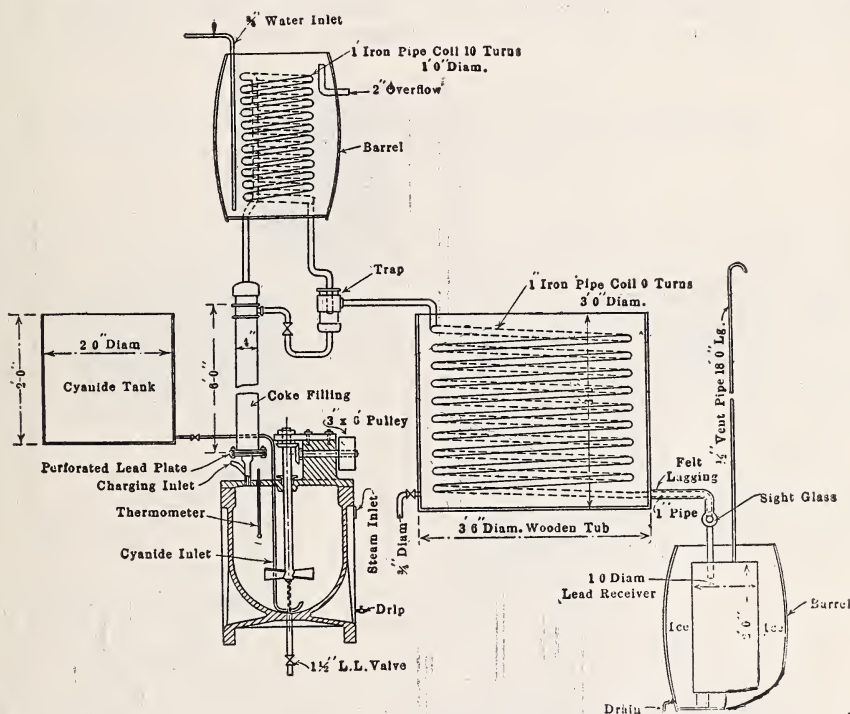


FIG. 1. APPARATUS FOR MANUFACTURE OF HYDROCYANIC ACID

saving in materials, apparatus and labor accompanied by a more efficient fumigation. It is also possible that hydrogen cyanide may replace carbon monoxide and other gases in fumigating vessels.

### METHOD EMPLOYED

The method employed, in brief, consists in adding sodium cyanide solution to dilute sul-

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phuric acid; the water vapor in the evolved gases is removed by fractional condensation, and the concentrated hydrogen cyanide is then condensed at atmospheric pressure. To expel hydrogen cyanide dissolved in the reaction mixture, the latter must finally be brought to the boiling point. Hydrocyanic acid forms dark tars with excess of sodium cyanide, and the cyanide is therefore added to the acid and an excess of the latter over the theoretical amount is employed. The residual liquor in the apparatus after the completion of the re-



large lumps of coke; the latter is supported by a perforated lead plate, placed at the bottom of the column and between the flanges so that it forms a gas-tight metallic gasket.

#### APPARATUS EXPLAINED

The reflux condenser is mounted above the column, and consists of about 30 ft. of 1-in. iron pipe, mounted in a half barrel and cooled by ice. Vapor from the column enters the top coil of the reflux; the lower coil leads into a separator, consisting of a tee. Vapor and condensate enter at the top of the tee through a long nipple; vapor leaves through the side opening, and condensate drains from the bottom, and back to the top of the column, through a trap.

The vapor outlet from the separator is piped to the main condenser; the latter is composed of 9 turns of 1-in. iron pipe, 3 feet in diameter. The coil is mounted in a wooden tub, and cooled by cracked ice.

The sodium cyanide container is a sheet-iron cylindrical vessel, with bottom outlet piped to the reaction kettle.

#### METHOD OF MANUFACTURE

The kettle is charged with 54 lb. of water and 54 lb. of 66 deg. B. sulphuric acid added, bringing the temperature of the mixture to about 70 deg. C. Forty pounds of sodium cyanide (96 to 98 per cent) are dissolved in 100 lb. of warm water in the sheet-iron container, which is then covered.

The condenser, reflux and receiver are packed in ice, the agitator started and the cyanide solution run into the kettle. The addition should take from  $1\frac{1}{2}$  to  $1\frac{3}{4}$  hours. Steam is then turned into the jacket of the kettle, and the mixture brought to the boiling point. The residue is discharged while warm, and the kettle and discharge lines flushed out.

When the receiver contains a sufficient amount of product, it is drained into an open

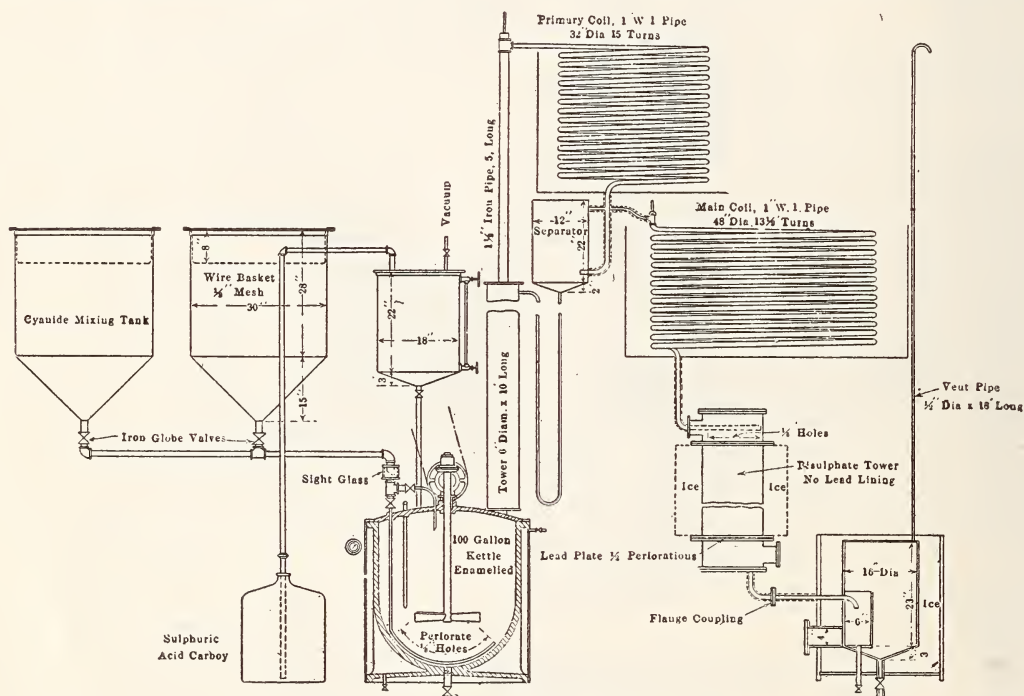


FIG. 2. A PROPOSED HCN APPARATUS

Condensate from the main condenser is received in a sheet-iron cylinder, 12 in. diam. x 24 in. The receiver is mounted in a barrel and provided with a bottom outlet and vent; the latter consists of a vertical length of  $\frac{1}{2}$ -in. pipe, the upper end bearing an inverted U. A sight glass is inserted in the line between the condenser and receiver. Product is charged in steel cylinder, with valves removed.

steel cylinder, previously weighed and cooled. The valve is then inserted, after applying red lead to the thread.

#### YIELDS AND PRODUCTION CAPACITY

An average yield of 78 per cent of the theoretical yield of hydrocyanic acid has been obtained. When the apparatus is properly manipulated the product runs from 90 to 95

per cent HCN. A production of 250 lb. per 24 hours has been obtained by the method herein described, and a total of 7000 lb. manufactured.

The approximate cost of production is calculated below:

	Cents per lb. of HCN.
Sodium cyanide at 31.5c.....	74.2
Sulphuric acid at 2c.....	6.4
Steam, power, ice, etc.....	10.0
Labor.....	14.3
Overhead and repairs.....	2.5
	<hr/> 107.4

The charges for power, labor, overhead, etc., can be materially reduced if units of larger capacity are employed.

#### PROPOSED IMPROVED PLANT

Fig. 2 is a drawing of a proposed plant in which various improvements are embodied.

Provision has been made for brine cooling and for more accurate temperature control.

As the stability varies with the purity of the product, a bisulphate tower has been introduced for the purpose of obtaining a more anhydrous product. The receiver is designed to separate any solids carried over from the tower.

In conclusion, the writers wish to express their appreciation of the many helpful suggestions offered by Dr. James R. Withrow, and also wish to thank George O. Kildow for his assistance in the work.

This work was started under the Bureau of Mines of the United States Department of the Interior, and was continued under the Research Division, Chemical Warfare Service.

Small Scale Production Section,  
Research Division, C. W. S.  
American University Experiment Station,  
Washington, D. C.

## Manufacture of Potassium Permanganate

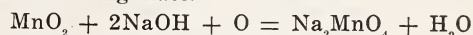
By RAYMOND B. STRINGFIELD\*

**D**URING the war, several plants were constructed in southern California to supply the demand for permanganates and the total tonnage produced was very considerable. No data, however, were available as to either scientific or operating details, and in consequence each plant had to work out its own salvation. Pressure of production necessarily greatly interfered with research, and cessation of hostilities, with the accompanying slump in the permanganate market, found many troubles still unsolved, and one by one the plants ceased operations. The interesting economic feature, however, is that no two plants had the same troubles, and had their combined knowledge been pooled the probabilities are that some if not all of the plants would still be operating profitably.

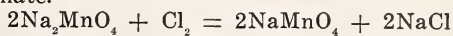
While potassium permanganate may be obtained in several different ways,<sup>1</sup> the sodium manganate process is the one which has been chiefly used in this country. The literature on the production of permanganate is scanty enough, and as practically no details of actual commercial operations have been published in English, it is hoped that the following notes taken from the author's experience with the industry in southern California will be welcome.

#### CHEMISTRY OF THE PROCESS

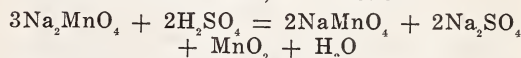
The sodium manganate process for the production of potassium permanganate may be divided into four main steps. Finely ground manganese ore and caustic soda, either with or without sodium nitrate as an oxidizer, are mixed and heated, either in a reverberatory furnace or a shallow iron pan, to form green sodium manganate.



This product is ground, dissolved in water, and the solution treated with chlorine and either sulphuric acid or carbon dioxide to convert the sodium manganate to sodium permanganate.



If no chlorine is used, the reaction



takes place, with the formation of only two-thirds the possible amount of permanganate and the precipitation of manganese dioxide. With the use of chlorine, the function of sulphuric acid or carbon dioxide is chiefly to neutralize the excess caustic soda, reducing the alkalinity, thereby allowing the more complete reversion of the manganate to permanganate.

The sodium permanganate liquor is freed from any manganese "mud."

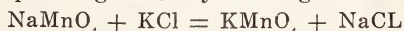
The liquor is evaporated until the bulk of other salts present have crystallized out. The theoretical amount of potassium salt is then

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<sup>1</sup>For electrolytic methods see CHEM. & MET. ENG., vol. 20, p. 387, and vol. 21, p. 680 (1919).



added, and the solution allowed to cool, potassium permanganate crystallizing out.



In the following description, the operation is not strictly that of any one plant, but details are combined from several plants in southern California.

#### FURNACES

The most important step in the process for making permanganate is the furnace reaction. Using caustic soda, equilibrium is reached in the reaction at a lower percentage of manganate than when potash is used,<sup>2</sup> but a considerable excess of alkali is necessary in either case, and economic conditions in this country favor the use of soda. Impurities in the ore affect the process in several ways. The presence of a small quantity of iron in the ore is beneficial, the reaction going slightly further toward completion, the iron perhaps acting as an oxygen carrier. Silica and alumina are detrimental, passing into solution later as sodium silicate and aluminate, their subsequent removal being an occasional source of trouble.

Although it is probable that further development would have been the roasting of the charge in comparatively thin layers in mechanically rabbled furnaces at a temperature below fusion, and with only air oxidation, the furnace operated most successfully was a gas-fired reverberatory furnace of the type shown in Fig. 1, operating at 980 deg. C. This furnace was built double, a crew of two men per shift handling the mixing, loading, rabbling and unloading for both furnaces.

Incoming manganese ore was passed through a Blake crusher, and then through a Herman ball mill, using 3-in. iron balls, the 80-mesh product being sent to storage. On account of inadequate grinding facilities, ground caustic soda was purchased in barrels. Sodium nitrate was delivered in 200-lb. (90.7-kg.) sacks.

The manganese oxides, "mud," recovered from the process were air dried on a cement floor, and returned to be used in a fresh mix.

The standard batch consisted of 325 lb. caustic soda, 225 lb. sodium nitrate and 350 lb. manganese ore (147.5, 102.1 and 158.2 kg. respectively). This was mixed in a small concrete mixer and loaded into the furnace with wheelbarrows, through charge holes in the top. It was then spread out with long-handled rakes, made from 4 x 6-in. (10.2 x 15.25-cm.) steel plates on 1-in. pipe, and as it fused was mixed frequently. When well fused, the mass was thoroughly stirred with compressed air by plunging a 1-in. (2.5-cm.) pipe on the end

of an air hose into various parts of the charge. This was repeated just before the furnace was discharged, and had the effect of increasing the percentage of sodium manganate about 1.5 per cent, and of leaving the mass spongy and much easier to grind. The charge was withdrawn by raking through the side discharge holes into wheelbarrows, from which it was spread on a brick floor to cool before grinding. Under normal conditions, eight charges could be handled in one furnace in twenty-four hours, making sixteen for the double furnace. On the charge given above, the average recovery from the furnace as crude green sodium manganate was 72 per cent of the weight of the raw charge. The "green" averaged 25 per cent sodium manganate, which is comparable to Australian practice.<sup>3</sup>

Under any operating conditions obtainable, the "green" was found to contain much sodium manganate, which decomposed on dissolving, throwing down a brown "mud," a mixture of manganese oxides. It was found that this "mud" could be air dried and worked into a fresh batch without lowering the quality of the "green." On account of the large amount of water in the "mud" it was not used alone, the mix being 325 lb. caustic soda, 200 lb. sodium nitrate, 250 lb. manganese ore, and 200 lb. air dried manganese "mud" (147.5, 90.7, 113.3 and 90.7 kg. respectively).

#### DISSOLVING AND CHLORINATING

The green manganate was passed through the same Blake crusher used for manganese ore, then through another Herman ball mill. The ground product was fed into a 700-gal. (2,650-l.) mechanically agitated dissolver, until the solution reached a specific gravity of 1.18, corresponding usually to the equivalent of 4.4 per cent  $\text{KMnO}_4$ . A greater density than this did not permit settling of the precipitated "mud." The liquor used for dissolving was the weak solution from the "mud" washing, carrying about 1.0 per cent  $\text{KMnO}_4$ . Into this dissolver, chlorine gas was run in the proportion of 1 lb. to every 4.45 lb. (0.45 to 2.01 kg.)  $\text{KMnO}_4$  in solution, giving from 55 to 60 lb. (24.9 to 27.2 kg.) per batch. Two chlorine cylinders were mounted on platform scales and the gas introduced through several small holes in a pipe in the bottom of the dissolver. No trouble was had with the chlorine, except that the evaporation would cause cooling, and it was necessary in cold weather to turn the steam hose on the cylinders to melt off the ice, and increase the pressure of the chlorine.

From the dissolver, the muddy liquor was run either to a sulphating tank, Fig. 2, where

<sup>2</sup>See the excellent work of Schlesinger, Mullinix and Popoff, *J. Ind. and Eng. Chem.*, vol. 11, pp. 317-328 (1919).

<sup>3</sup>See *MET. & CHEM. ENG.*, vol. 18, p. 546 (1918).

strong sulphuric acid was added, or to a carbonation tower, where it was treated with carbon dioxide gas. In either case, the alkalinity of the solution was reduced to less than 1.0 per cent free NaOH, this point being easily controlled, with a little experience, by the color of the liquor, the green of the manganate changing to the full permanganate color at about 1.5 per cent alkalinity. The effect of the chlorine is apparently to form hypochlorite, which remains as such until the alkalinity is reduced, when it oxidizes the manganate

silica and alumina in the solution with it. This is especially true when carbonated liquor is used, sulphated liquor carrying a much larger percentage of impurities in solution. If the liquor is excessively alkaline, the salt is very fine, and tends to form hard cakes in the centrifugals, making thorough washing very difficult. On the other hand, too low an alkalinity causes the formation of a hard scale on the coils. As the alkalinity increases, due to concentration, the tendency for the permanganate to revert to manganate increases, and above

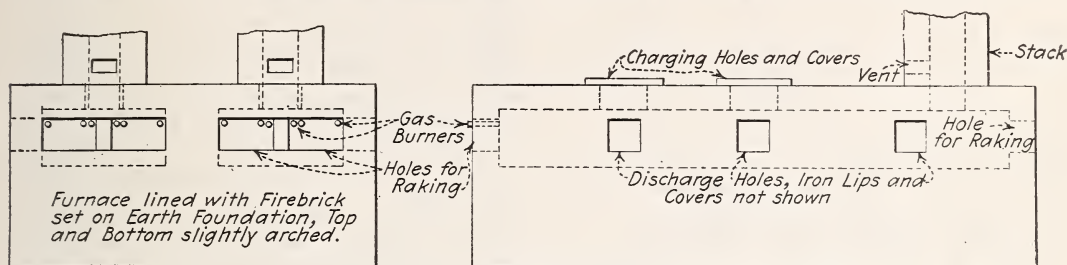


FIG. 1. FURNACE FOR SODIUM MANGANATE, 12 x 18 FT.

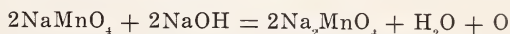
to permanagate. The chlornated liquor should be neutralized as soon as possible, and should not be exposed to the sunlight on account of the decomposition of hypochlorite and evolution of oxygen. The possibilities of electrolytic oxidation of the manganate in a suitably designed cell are very interesting.

The sulphated liquor was run to one of a series of four settling tanks, from which, after the mud had settled, it was decanted to a fifth tank, and the clear liquor from the top of this tank run over a weir to a "soda liquor storage." Both steel and concrete were found to be suitable for storage, little corrosion taking place as long as the liquor was alkaline, although the concrete was slowly affected. The mud was washed by counter-current decantation, and finally sent to the drying floor. This washing system could very profitably be replaced by a system of Dorr thickeners.

#### EVAPORATION

From storage, the "soda liquor" was pumped through a small measuring tank to open steel pans, where it was evaporated by means of steam coils immersed in the liquor, using steam at 60-lb. pressure (4.2 kg. per sq.cm.). As the solution became concentrated, the other salts present, being less soluble than sodium permanganate, were thrown down and were raked from the bottom of the kettles, centrifuged as dry as possible, washed with hot water, and sent to a salt dump. The handling of the salt is influenced considerably by the alkalinity of the liquor. When of proper alkalinity, the salt comes down granular, does not scale the coils, and carries most of the

5.0 per cent NaOH is liable to cause trouble, the probable equation being:



The kettle men were taught to test their own samples by the procedure given later, and when the liquor reached a concentration equivalent to 14.0 per cent potassium permanganate, an amount of potassium sulphate or chloride equivalent to the permanganate present was placed in a wire basket and lowered into the boiling solution. This dissolved rapidly, and the solution was then drawn off to shallow iron coolers holding about 400 gal. each. These were supported so as to have free circulation of air, and cooled in four to six hours. After drawing off the cool mother liquor, the crystals were raked into a centrifugal, spun free of liquor, washed with cold water, recrystallized if necessary, dried on screens in a current of warm air, and packed in containers for shipping.

In connection with the crystallization, some interesting solubility effects are observed which deserve much further study. Various mixtures of chlorides, carbonates and sulphates are observed to repress the solubility of permanganate greatly, a mother liquor of 3.0 per cent being common, and 1.0 per cent not uncommon, against a normal solubility of potassium permanganate in pure water of 6.0 to 7.0 per cent. It should also be noted that the true color of potassium permanganate crystals is a brownish black. In former years, the trade has demanded purple crystals. The color was due to a film of decomposed permanganate on the surface. This was caused



by the method of drying, and decreased the purity of the crystals 0.2 per cent or more.

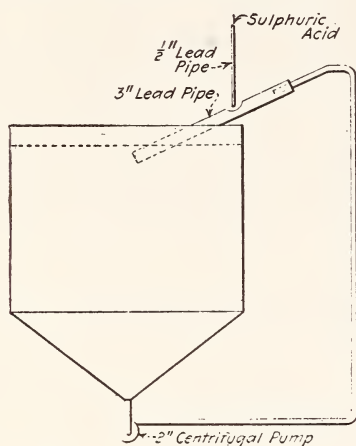


FIG. 2. DETAIL OF SULPHATING TANK

Most users have now become accustomed to the black crystals, and demand them as the purer product.

#### LABORATORY CONTROL

As mentioned before, a simple method was developed for the analysis of the ordinary permanganate liquors, and the kettle men were taught to make this determination on the soda liquor going to the kettle (to calculate the amount of potash to be added) and on the concentrated "hot liquor." This lessened the labor in the laboratory very materially, and made it possible to run it one shift without delaying plant operations.

As several of the analytical methods used have not been published, a résumé of these may be of interest.

**Permanganate.** For purposes of comparison, all results, even on soda liquors, were expressed in terms of potassium permanganate.

**On Liquors, Salts and Raw Crystals.**—Ten c.c. N/10  $\text{FeSO}_4$  containing 19 per cent  $\text{H}_2\text{SO}_4$ , was titrated cold with a solution of the unknown permanganate, and results read from a table based on the following: For strong liquors, dilute 10 c.c. to 500 c.c. then

$$\text{per cent } \text{KMnO}_4 = \frac{158}{\text{c. c. titration}}$$

For weak liquors, salts and raw crystals, use larger or smaller quantities and correct the result accordingly.

**On Green Manganate.**—Dissolve 5 to 10 g.  $\text{NaHCO}_3$  in 200 c.c. of water, add 5 g. finely ground manganate, stir until dissolved, dilute

to 500 c.c., settle out  $\text{MnO}_2$ , and titrate with this solution as above. Multiply result from table by 3 to give total yield of permanganate obtainable with complete chlorination, since with this method three molecules of manganate give only two of permanganate and one of manganese dioxide.

**On Potassium Permanganate, U. S. P.**—Dissolve 0.750 g. in 200 c.c. hot distilled water in a 400-c.c. beaker, add 5 c.c. 1:1  $\text{H}_2\text{SO}_4$ , and pipette in very carefully 25 c.c. N oxalic acid. Stir until the  $\text{MnO}_2$  formed is all dissolved, and titrate the excess oxalic acid with N/10  $\text{KMnO}_4$ . At the same time, run a standard on 0.750 g. of potassium permanganate of known purity. This was prepared by recrystallizing U.S.P. potassium permanganate twice from distilled water, and drying in an air oven at 105 deg. C. On this product, water insoluble was determined on a 10-g. sample, and purity called 100.00 — insol<sub>10</sub> which was usually over 99.95 per cent. To calculate results, using a slide rule, let  $t_1$  = back titration of standard, and  $t_2$  = back titration of sample. Ten purity of the sample =

$$\text{per cent standard} = \left( \frac{t_2 - t_1}{237} \right), \text{ i.e.}$$

$$99.95 = \left( \frac{14.3 - 13.0}{237} \right) =$$

$$99.95 - 0.55 = 99.40 \text{ per cent}$$

Duplicate determinations by this method check easily to 0.05 per cent, which is a much

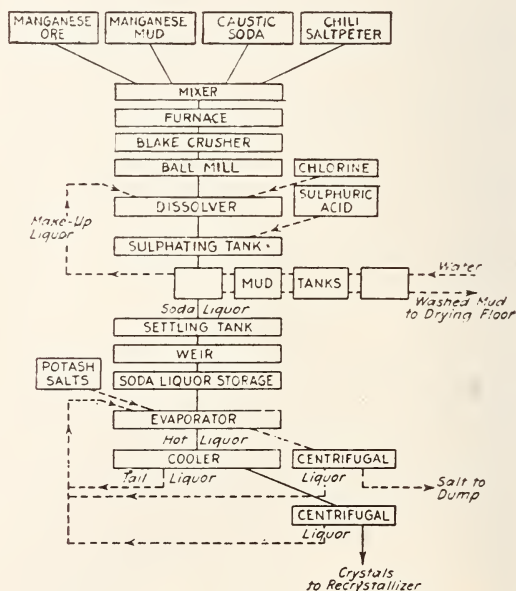


FIG. 3. FLOW SHEET, MANUFACTURE OF PERMANGANATE

greater accuracy than can be obtained by the method of the U.S.P.

<sup>4</sup>Credit for this method belongs to R. W. Poindexter, Jr., of Poindexter & Co., whose suggestions were responsible for its development.

**Alkalinity** (Causticity due to NaOH).<sup>5</sup> On any strong liquor, dilute 25 c.c. sample to 250 c.c., and of this, take 10 c.c., decolorize with neutral  $\text{H}_2\text{O}_2$  dropwise, filter with suction on an asbestos Gooch crucible, wash, keeping volume as low as possible, precipitate carbonates and sulphates with 10 c.c. of 10 per cent  $\text{BaCl}_2$ , filter, wash and titrate with  $\text{N}/4$   $\text{HCl}$ , 1 c.c. = 1.0 per cent NaOH. On weak liquors,  $\text{H}_2\text{O}_2$  and  $\text{BaCl}_2$  may be added in same solution and filtered together.

#### RESEARCH WORK NEEDED

Several phases of this process present opportunities for interesting and commercially important research work. Much of this work requires equipment usually found only in a good university laboratory, and in case of an opportunity to engage in such work, the following suggestions are offered.

1. The effect of various proportions, temperatures, impurities and catalyzers on the furnace reaction between caustic soda and manganese ore.

2. Solubilities and phase rule diagrams for mixtures of the chlorides, sulphates, carbonates and permanganates of sodium and potassium.

3. The development of a suitable cell for the electrolytic oxidation of sodium manganate to permanganate.

4. Decomposition of permanganate solutions in the presence of  $\text{MnO}$ ,  $\text{MnO}_2$ , etc.

5. Best conditions for the elimination of silica and alumina from permanganate solutions.

6. Conditions affecting the reversion of permanganates to manganates in alkaline solutions.

#### SUMMARY

1. Details for the manufacture of potassium permanganate as carried on in southern California have been given, with analytical methods used in controlling the process.

2. A number of lines of research work are suggested.

Los Angeles, Cal.

## The Function of the Chemical Engineer in the Biscuit and Cracker Baking Industry

By O. C. F. LIPPERT

Chemical Engineer, the George H. Strietmann's Sons Co.

THE idea of having a chemical engineer associated with the organization of a biscuit and cracker bakery is a modern one. This is due to the fact that biscuit and cracker bakeries until recently have been rather successfully conducted by the "rule of thumb" methods.

The industry for the most part was made up of very small units in which it was possible for one or two men to successfully make and bake all the products by a sort of intuition, just as the housewife supplies the home with good bread and cake. That is, if she is asked to tell how she makes her products, she will somewhere in her instructions for making, or in her recipe, say: "I add so much of this or that until I get a certain taste," or else she will say: "I bake it until it gets such and such a color."

In a similar manner in the past and to some extent even today, the foremen of the various departments had and have that intuition which permits them to turn out a product which cannot be readily duplicated, even by their own assistants.

When one of these small units reaches a certain size, it becomes necessary that the prod-

ucts which the firm produces maintain a certain standard. Unfortunately it becomes impossible to maintain this standard when the responsible foreman is incapacitated. This is disastrous to the marketing and sale of the product and so the slogan of the sales department is "Uniformity." In the home or smaller concerns the problem would be met by waiting until the return of the party with the "gifted or inspired method of procedure." Where the units or plants are large, it is readily admitted that this is entirely impractical. Accordingly it becomes necessary to devise means and methods to bring about this uniformity. In this connection the services of a chemical engineer are most valuable, as his training, devoted to the study of materials and to methods of manufacture, fits him for undertaking work of this nature.

His work almost automatically divides itself into three main divisions which may be characterized as studies of

(a) raw materials,

(b) methods of manufacture,

(c) finished products and industrial engineering.



### RAW MATERIALS

The problem of studying raw materials as used in the baking industry with reference to uniformity is complex. There is probably no industry which uses so many varieties of raw materials in so many combinations. Also, the raw materials are, for the most part, organic in nature and complex in structure, as the following list will show: Flour, butter, lard, shorteners, vanilla and flavoring extracts, eggs, milk, sugar and others. The inorganic raw materials, such as salt, sodium bicarbonate, do not present any difficulties. However, ammonium carbonate, the associate of sodium bicarbonate as to functioning, has presented rather interesting studies from time to time owing to its complex nature.

### METHODS OF MANUFACTURE

Topics in this group are:

1. The proper sequence of raw materials in mixing.
2. The physical condition of the raw materials before mixing.
3. The manner of mixing.
4. The conditioning or aging of the mix.
5. The treatment or preparation of the dough for the cutting machine.
6. The quantity of heat used.
7. The quality of heat used (including kind and temperature).
8. The method of baking (whether directly on the ovenpans, or on wire mesh pans, or on separate greased pans).
9. The subsequent cooling of the product.
10. The time elapsed from leaving oven until in container.

Not every problem required a study of all of the above topics, but all required taking into consideration at least the greater number of them.

### FINISHED PRODUCTS AND INDUSTRIAL ENGINEERING

Concomitant with methods of manufacture, problems of industrial engineering are met with such as:

1. Time and motion studies of operations.
2. Stock arrangements.
3. Routing of materials (both raw and finished).
4. Costs and production.
5. Mechanical problems of equipment.

### TYPICAL ANALYSIS NEEDED IN THE BAKING INDUSTRY

In order to give some idea as to the nature of the raw materials studies, the following is presented.

The main raw material used in the baking industry is flour, which is supplied in sacks of 98 lb. and 140 lb. (usually the latter). It is stored on platforms or trucks, twenty-one sacks to a platform in layers of three sacks each. The problem of getting representative samples and keeping track of the various lots as received and analyzed was rather annoying, as it was of little importance to the stores department workmen to keep supplies according to lots. It was met by tagging each platform with a serial number and using the well-known butter or lard "trier" or "thief." It was found that the trier gave a conical sample extending from the outside of the sack to the inside or center. In this way, the sample contained flour which had been subjected to atmospheric conditions as well as flour which had been protected from same. By taking samples from several sacks in proportion to the size of the lot of flour and mixing these sack samples, a very representative lot sample was obtained.

The next problem was, What kind of analysis should the flour be subjected to, consistent with time, cost and results?

The following analyses are typical of flour as used in the baking industry and as submitted by wheat and flour-testing laboratories:

	Straight Per Cent	Patent Per Cent	Patent Per Cent
Moisture.....	12.50	11.18	11.70
Fat or oil.....	1.12	0.98	1.35
Ash.....	0.564	0.508	0.488
Absorption.....	57.00	56.00	56.55
Color.....	100.00	104.00	101.00
Gluten (dry).....	8.38	9.49	10.36
Protein (5.7 X N).....	9.22	10.28	11.55
Quality of gluten.....	100.00	94.70	101.50

Sometimes the additional information of loaf value (expressed in per cent) is given.

### CRITICAL STUDY OF THE ANALYSES FOR USE IN THE CRACKER-BAKING INDUSTRY

A critical study of the analyses for use in the cracker-baking industry as to the importance of the individual items, consistent with time, cost and results, led to the following conclusions:

1. That the moisture, gluten, absorption, protein and ash determinations were worth the time and cost.
2. That the fat determination was not worth the time and cost.
3. That the loaf value was not directly applicable in the cracker and cake industry and hence not worth the time consumed in obtaining it.
4. That the color and quality of gluten determinations were of some value.
5. That some supplemental test or deter-

mination would have to be made which would give the same information to the cracker baker about the quality of gluten that the loaf value does to the bread baker.

6. That this test must be carried out in conjunction with some of the other tests.

The bread baker bakes one kind of product—that is, he bakes different kinds of bread—but he is not using his flour in as many different formulas nor is he using it with as many kinds of ingredients.

#### IMPORTANCE OF DETERMINING THE VALUE OF GLUTEN AND THE METHOD OF ITS DETERMINATION

The problem narrowed down to determining the value of gluten as gluten alone and the effect of heat on the gluten, i.e., of determining what was afterward called the expansion test.

At the present time no method is known by which proteins or gluten may be isolated by chemical methods. However, the physical method, of washing out the starchy part of flour, is very applicable, especially so since it can be carried out with rapidity. Furthermore, the absorption value can be previously determined and subsequently the appearance and elasticity of the gluten noted and examined on the same sample.

The method of procedure for obtaining the absorption value and washing out of the starchy material is as follows: 33.33 g. of flour is weighed into a beaker and 15 c.c. of cooled distilled water is added from a burette. It must be remembered in connection with the washing out of the starch that the temperature of the water is of importance, i.e., must be kept cool. Then  $\frac{1}{2}$  c.c. of water at a time is added until a dough of proper consistency is formed. The number of c.c. of water used multiplied by 3 equals the absorption of the flour for water.

#### REGULATION OF WATER FLOW

Enough water is now added to cover the dough and same set aside for 1 hr., after which it is washed out over a screen of bolting cloth, using cooled (in summer cold) water, until free from starchy material. Care must be exercised not to have the water flowing too fast, as it tends to divide the gluten into small particles which are hard to incorporate with the main portion. Care must also be taken not to extend the washing-out process over too long a period of time, as this causes the gluten to adhere to the fingers. Any loose or small pieces of gluten which have been caught on the bolting cloth screen can be gathered by using the main ball as a swab. The screen is made by fastening silk bolting cloth (125 mesh to the lineal inch) into the

largest size obtainable embroidery frame. The gluten thus gathered into one ball is put in a beaker using fresh cooled water and allowed to stand for an hour, after which it is observed as to its elasticity and quality, which are determined by physical examination.

Glutens of excellent quality will have a light or creamy color, will remain solid and will be elastic. There is, however, a difference in the elasticity of excellent quality gluten. Some stretch very readily without breaking, while others offer more resistance. This aids in a preliminary way in determining the use of a flour, i.e., whether it is adapted for crackers or cakes.

#### METHOD OF DETERMINING THE HEAT ACTION ON GLUTEN

The following method was developed in determining the heat action on gluten and has been termed the "expansion test": The moisture from the isolated gluten is removed by pressing the gluten between the palms of the hands and the fleshy part of the thumb. Care must be taken to have the hands cool (which is usually accomplished by allowing water to run over the wrists). The hands must be frequently dried during this operation. The gluten is then rolled into a ball and transferred to a clean, previously weighed, zinc plate about 2 in. square, which is then placed in an electrically heated oven or furnace, where a temperature of 158 to 160 deg. C. is maintained for 18 min. At this temperature and for this time the best expansion of the gluten is obtained. It is then transferred to a drying oven maintained at 100 deg. C. for a period of 16 hr. (usually over night), then weighed and dried to a constant weight at hourly intervals. It has been found that all the moisture has been expelled in the 16-hr. period when the test is conducted as above.

#### METHOD OF MEASURING EXPANSION

The measuring of the expansion is accomplished as follows: The gluten ball is carefully removed from the zinc plate (zinc plates are used because the adhesion of gluten to zinc is less than in the case of other metals or glass) and placed in a  $2\frac{1}{2}$ -in. cubical measuring box with sliding lid. Seeds of fair size (such as hemp) are added (from a graduated cylinder filled with the seed and whose cubical contents equal that of the box) until the box is filled. The seeds remaining in the cylinder give the cubical contents of the volume occupied by the gluten ball. The volume thus obtained, divided by the number of grams of dried gluten, equals the expansion per gram of gluten, which when multiplied by the per cent of protein obtained by chemical methods equals the total expansion volume of the gluten in terms of c.c. per 100 g. of flour.



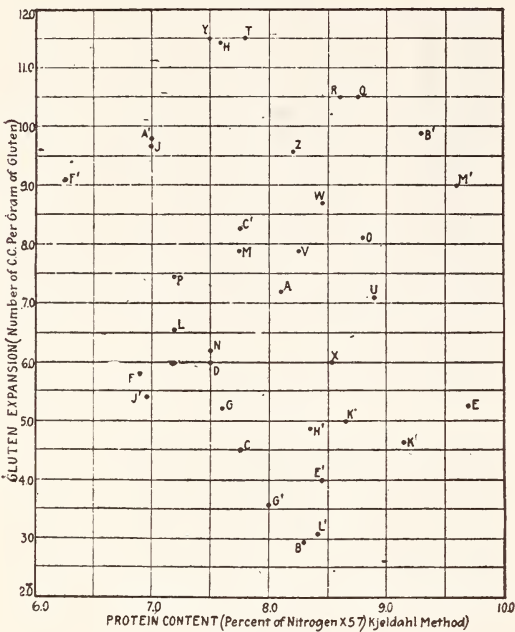


FIG. 1.

TABULATED AND PLOTTED RESULTS OF FLOUR ANALYSES

A statistical study is then made every season (usually about August, when the new flour comes in) of the expansion factor with reference to the protein, gluten (by washing-out method) and the ash determinations. Table I gives the information in tabular form, supplemented by curves and comments thereon, of a typical season.

The curve sheets show clearly the variations encountered in flour analysis. Fig. 1 illus-

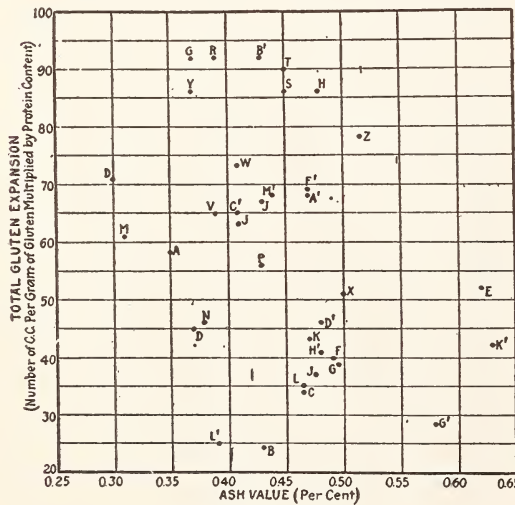


FIG. 2.

trates the variation met with in protein content and gluten value. Fig. 2 combines the data as given in Fig. 1 with the ash value, which is the index as to how the wheat was milled to produce the flour.

A high-grade flour most generally has a low ash value. A 40 per cent patent means that only 40 per cent of the wheat was used (i.e., the best part), while a 60 per cent patent would be milled from 60 per cent of the wheat and hence would contain more mineral matter, with a resulting higher ash content. It has been observed, however, that flour obtained

TABLE I.

Lot Symbol	Protein in Per Cent (5.7 X N)	Gluten in Per Cent	Gluten Expansion in c.c.	Gluten Expansion per g. of Gluten (calc)	Total Expansion per 100 g. of Flour (calc.)	Ash Value Per Cent
A	8.07	9.30	22.3	7.20	58.20	0.35
B	8.32	10.65	10.8	2.95	24.60	0.43
C	7.73	9.45	14.1	4.48	34.60	0.47
D	7.51	9.15	15.0	6.00	45.00	0.37
E	9.69	11.10	19.5	5.27	51.00	0.62
F	6.90	7.65	14.8	5.80	40.00	0.49
G	7.60	7.95	13.8	5.22	39.60	0.39
H	7.55	8.40	32.0	11.40	86.00	0.48
J	7.00	7.35	23.5	9.60	67.00	0.43
K	8.66	9.75	16.2	5.00	43.30	0.47
L	7.19	8.70	19.0	6.56	47.20	0.35
M	7.74	9.30	24.5	7.90	61.20	0.31
N	7.50	7.00	14.5	6.18	46.40	0.38
O	8.79	8.15	22.0	8.08	71.00	0.30
P	7.20	6.77	16.8	7.45	53.60	0.43
Q	8.74	10.80	37.7	10.45	91.50	0.37
R	8.59	10.50	36.6	10.45	91.50	0.39
S	8.50	10.20	30.0	10.20	86.80	0.45
T	7.80	9.90	38.0	11.50	89.60	0.45
U	8.90	9.15	21.6	7.10	63.20	0.51
V	8.27	9.00	23.8	7.86	65.00	0.39
W	8.46	10.05	29.0	8.70	73.50	0.41
X	8.55	10.50	21.0	6.00	51.30	0.50
Y	7.51	9.75	37.5	11.50	86.40	0.37
Z	8.18	10.35	33.0	9.56	78.40	0.52
A'	6.96	8.40	26.3	9.80	68.00	0.47
B'	9.29	10.50	34.7	9.90	92.10	0.43
C'	7.75	8.40	20.9	8.22	63.60	0.41
D'	10.46	11.40	17.0	4.40	46.00	0.48
E'	8.41	10.05	15.0	4.50	37.80	0.39
F'	6.25	6.90	25.3	11.00	68.80	0.47
G'	7.92	9.90	10.6	3.56	28.20	0.58
H'	8.34	8.40	13.6	4.85	40.50	0.48
J'	6.98	7.65	13.7	5.36	37.40	0.48
K'	9.17	10.55	16.3	4.64	42.60	0.63
L'	8.41	9.36	28.5	3.04	25.60	0.39
M'	7.59	10.50	31.5	9.00	68.20	0.44

from wheat grown on the Pacific Coast has a high ash value due to the soil in which the wheat is grown.

The total gluten expansion value gives with one figure the combined quality and quantity value of the gluten. Having worked out, at the beginning of the season, charts similar to those given, it is a rather easy matter on subsequent analyses for the same reason to determine just where a flour belongs and what it can best be used for, crackers or cakes, and also what kind of cakes.

The absorption value tells how much water to use in your mixes and the moisture determination tells how much water you are paying for.

In a similar manner, standard specifications were worked out for other raw materials. Chief among these were:

1. Butter, lard and shorteners; in which it was found advisable to make melting point, refractometric, moisture, ash (including salt), casein determinations; obtaining fat by difference. Special attention must always be paid to color, taste and odor.

2. Milk products and milk powder; make ash, moisture, fat (Babcock method—Leach) determinations.

3. Molasses, syrups, sugar; make moisture, invert sugar and sucrose determinations.

4. Flavoring extracts; make specific gravity determinations and observe taste.

5. Baking powders; make acidity tests and determine starchy material.

The most striking example of the methods of manufacture studies was "Ammonium Carbonate Versus Ammonium Bicarbonate." Merck's 1907 Index gives the following information about the two salts:

*Ammonium Bicarbonate*—Large, transparent crystals, soluble in water and alcohol. Decompose at 60 deg. C.

*Ammonium Carbonate*—Mixture of ammonium bicarbonate and ammonium carbamate. Crystals, white, effloresce in air, stringent ammonia odor, sharp saline taste, soluble in five parts water at 15 deg. C. Decomposed by hot water.

Analyzing the samples for ammonia content, it was found that the commercial products as furnished to the baking trade gave the following figures: Ammonium bicarbonate, 20.86 to 21.05 per cent. Ammonium carbonate varied from 22.50 to 25.60 per cent.

It will be readily seen that the ammonium carbonate does not aid in producing uniformity of product, as it is itself quite variable in constitution. It is true that as to ammonia content it is stronger and hence would be more economical, as its function is to produce volumes of ammonia gas. An attempt was made to get the same baking results by using ammonium bicarbonate in sufficient quantities to equal the ammonia content of ammonium carbonate. The results, however, did not equal those ordinarily obtained. It was then decided to investigate the manner of mixing and also the baking. This investigation showed that certain kinds of cakes must have a leavening agent which is capable of acting quickly upon the application of heat. This was found to be true of ammonium carbonate, as it is more unstable than ammonium bicarbonate.

#### TEST OF ACIDITY IN SPONGES USED IN THE BAKING INDUSTRY

Another example of this type of studies is "Acidity in Sponges in the Making of Crackers."

By "sponge" in the baking of crackers is meant that portion of the raw materials which is mixed in advance with the fermenting agent. This sponge is allowed to stand for a long time, becoming acid due to the fermentation. This acidity is neutralized with sodium bicarbonate when the remainder of the raw materials are added to make the dough, which in turn goes through a fermenting period of short duration. Experience has shown that when all other figures or factors are constant, there has been developed an empirical relationship between the temperature of the sponge just before mixing and the amount of soda to be added. When other variables enter into the mixing conditions, erratic temperatures are obtained. To take these variables into consideration, the following chemical method was developed. The sponge is sampled and exactly 20 g. weighed out into a white enameled dish and distilled water added to dissolve the sponge thoroughly. Standard alkali is run in from a burette to neutralize the acidity, using phenolphthalein as an indicator. The burette is so graduated as to read per cents directly. A table furnished to the workman performing this test tells how much soda to add. This table was prepared in the laboratory making acidity determinations on the sponge and also on the finished products resulting therefrom. In this way any erratic temperatures are subjected to chemical checking.

The finished product and industrial engineering studies were more closely correlated than in the two preceding groups and accordingly do not offer isolated examples.

In the cracker industry we have the following factors entering into production and costs: In the making of approximately two hundred different kinds of finished products, sixty different materials are used. These products are made on ten different ovens or machines. Each product has its own die or cutter for cutting out the cake. Each dough has its ideal speed at which the cutter will work effectively. There is also an ideal time for baking and a certain number of operators are required for each product. The finished cakes will average so many to a pound, depending upon the cake. Similarly, there is an average weight for each packing container (large can, small can, wood boxes, barrels, drums and cartons), and there is a certain speed of packing, depending upon the size and nature of the product.

All of the above factors vary from day to day, and as a result the determination of



standards representing ideal operating conditions was an extremely difficult task.

The standard method adopted by which to measure production and cost standards in the cracker baking industry requires a knowledge of the following:

1. Determine the number of cakes cut out with every stamp of the cutter.

2. Determine the ideal speed (ideal referring to speed at which the resultant product is best obtained) at which to operate the cutter, i.e., cuts per minute.

3. Determine the average number of cakes per lb.

4. Determine the minimum number of operators who can effectively turn out the product.

The above applies to manufacturing departments as contrasted to packing departments.

In the packing departments, it was necessary to set up an individual standard for each product in each and every kind of packing container.

Since the goods are sold on a pound basis, it is evident that the cost standard must include pounds in its expression or terms. Furthermore all production and cost standards involve time. If the machine cost variance is great and the machines are operated by the same number of operators, then the machine hour basis is most applicable. In the cracker-baking industry the variance is found in operators and not in the cost of the machines. Hence the most applicable and accurate production standard is expressed as pounds produced per operative hour or the pounds produced per person per hour. For cost work, it takes a more convenient form, its reciprocal, or part of an operative hour required to produce 100 lb.

In the course of a day there is manufactured approximately fifteen different styles of goods, each with a different rate of production as follows:

Product A.....	100 lb. per person per hour
Product B.....	174 lb. per person per hour
Product C.....	102 lb. per person per hour
Product D.....	170 lb. per person per hour
Product E.....	147 lb. per person per hour

The respective cost standards are:

Product A.....	1.000 operative hr. to produce 100 lb.
Product B.....	0.575 operative hr. to produce 100 lb.
Product C.....	0.980 operative hr. to produce 100 lb.
Product D.....	0.590 operative hr. to produce 100 lb.
Product E.....	0.680 operative hr. to produce 100 lb.

The production rate of "lb. per operative hr." is computed according to the following equation:

$$\frac{\text{Pounds per operative hour} = \text{Cakes per cut} \times \text{cuts per min.} \times \text{operating min. per hr.}}{\text{Number of operators} \times \text{cakes per lb.}}$$

It was necessary, in installing a system of this design, first to explain thoroughly to de-

partment heads just how the reports were to be made out—that is, to distinguish between direct help (working on the particular machine) and indirect help (foreman, mixers and others who are intermittently working on several varieties of goods at one time), to take accurate speeds and keep accurate time, so that the data represented true and actual conditions; secondly, to explain to the cost department assistants how to interpret correctly the data submitted and compute the production rates as well as to detect inconsistencies. For a certain period of time it was necessary to make computations of standards daily on each and every run in order to check up intentional carelessness on the part of some in assembling the data; after which it was possible to fix a certain standard rate of production. By dividing this standard rate of production for any given variety into the total pounds produced in any day, it is possible to obtain the time equivalent in operative hours of direct help of work produced. Dividing this time equivalent by the actual time spent by the operatives on the particular run, the efficiency of the run is obtained.

#### STANDARDS REPRESENTATIVE OF OPERATING CONDITIONS

If the efficiency thus obtained is abnormally low, then it is due to one of two conditions: (1) abnormal operating conditions (necessitating a change of standard), or else (2) indifference on the part of the operatives to maintain the production standard as set. In the case of abnormally high efficiencies, the standard is set too low, or else the data as submitted do not represent true conditions. In this way the standards receive constant checking and represent actual or operating conditions.

In the packing department it often occurs that several kinds of packages are being packed at one time off one run, and therefore the best method to set standards was found to be by making time and motion studies for each and every piece and container. This requires careful and keen observation and unprejudiced conclusions. In a few instances it was found that group studies could be made.

Time and motion studies in the cracker industry on packing operations are quite different from studies in the machine shops, due to so many variables and also due the fact that the operators are girls unfamiliar with time and motion study work; hence it was most difficult to have them understand just what was wanted.

#### FACTORS IN TIME AND MOTION STUDIES

The following are the observations which must be made in connection with time and mo-

tion studies of packing operations in the cracker-baking industry:

1. How are crackers brought to the packers?  
(On conveyors or on trays in stacks.)
2. How are packing containers supplied to the packers?
3. Do packers pack from conveyors?
4. Movement of conveyors—intermittent or regular?
5. Kind of product—cracker or cake?
6. Size of product?
7. Shape of product?
8. Thickness of product?
9. Do products stick to conveying pans?
10. Are stackers required?
11. Time to pack each individual layer.
12. Time to face front of containers.
13. Number of crackers or cakes per row.
14. Number of rows per layer.
15. Number of layers per container.

#### DETERMINATION OF PLANT EFFICIENCY

Having determined the standards, the efficiency is determined as follows: The weight of goods packed in style I container is divided by the standard (for that particular container), giving the time equivalent for style I; similarly style II is treated, etc. Then the time equivalents expressed in operative hours of work produced of all the styles of containers for one variety of product are added and the sum is divided by the total number of operative hours of direct help, giving the efficiency. It is more difficult to detect errors in setting standards in the packing operations, as the effect of any single standard is masked in arriving at the efficiency per cent.

The time equivalents or standard operative hours of work produced for all varieties in a department are totaled for a given period of time (usually a month). These totals are then divided into the departmental labor charge (includes both direct and indirect help for the same period of time), giving the operating labor cost per operative hour. Similarly, the same totals are divided into the departmental burden, giving the burden cost per operative hour.

In calculating the cost of labor and burden

on any piece or variety of goods, the cost unit (part of an operative hour required to produce 100 lb.) is multiplied by the rate per operative hour, giving the cost per 100 lb.

#### CONCLUSION

The difficulties in installing a system of this kind are the usual ones met with in installing any new industrial engineering system, namely,

1. Convincing every one concerned as to the importance of co-operation.
2. Designing suitable forms, reports and cards.
3. Interpreting and straightening out details which cannot be covered by a set of general instructions.

It must be remembered that owing to seasonal variations in the raw materials, factory methods are constantly changing, and accordingly the members of the cost department must always be on the alert to detect any irregularities.

This system has been in operation for two years and has been developed to such an extent that standard costs as calculated are proved against the actual departmental costs with only a very small percentage of variance. In this way it is possible to ascertain just what goods are creating and what ones are not creating departmental profits and also to anticipate new production costs very accurately.

In connection with the time studies on packing operations, a piece rates schedule was set up which increased production without increasing costs. This schedule is closely co-ordinated and consistent with the cost standards as set.

Summarizing the results of this investigation it has been shown that some of the functions of the chemical engineer in the cracker and biscuit baking industry are:

- (a) Setting up standard specifications for purchase and control, checking of raw materials used.
  - (b) Investigating methods of manufacture and giving technical assistance.
  - (c) Solving industrial engineering problems.
- Cincinnati, Ohio.



## Chemical Warfare—A New Weapon

BY ELLWOOD HENDRICK

**I**N August, 1917, Brigadier General Amos A. Fries, of the U. S. Engineers, was appointed to command the chemical warfare service of our Army in action. He has lately returned to the United States, and it was the privilege of the writer to spend a couple of hours in discussion with him concerning gas warfare and the chemical wing of the service. Gen. Fries has been awarded the rank of Commander of the Legion of Honor by the French Government.

The opinion seems to prevail generally that the use of poison gas, launched in breach of faith by the German High Command, has reached an end for all time; that by general agreement in convention it will no longer be endured, and that it is to be classed with the many practices of violence and debauchery of which the German army was guilty.

This is not in accord with General Fries' opinion. The Allied troops used chemical warfare in constantly increasing measure because it is an effective weapon. On the other hand atrocities were neither practiced, encouraged, nor permitted. It is General Fries' belief that the use of other chemicals besides shot and shell, having been introduced into the art of war, can never be eliminated. The situation is somewhat like that when gunpowder was introduced, and universally frowned upon as unfair and unsportsmanlike; yet it has endured.

### WHY CHEMICAL WARFARE WILL NOT BE PERMANENTLY SUPPRESSED

The principal reasons why gas and chemical warfare is unlikely to be permanently suppressed are because

It is the most humane method of fighting, if both sides are prepared for it, while

It is the most deadly of all methods to the side that is unprepared.

The "humanity" of poison gas we shall consider shortly; the first point is that the army that is prepared against it is unlikely to be severely injured, while that which is unprepared is almost certain to meet defeat in an attack. Now, wars are usually caused by the breach of agreements, and it is seldom that a nation at war trusts its enemy. And if the enemy by the use of chemical warfare is able to win, then its opponent will have to be prepared. War has not yet reached the stage of the code duello, whereby an impartial umpire may step in and declare the fight off if unfair practices are employed. So the only safety against defeat is to be prepared against chemical attack. This takes a long time and pecu-

liar training, while most wars are of shorter duration than that with which we have lately been engaged. The old military axiom of safety in preparedness still holds good. When the Germans launched their first clouds of chlorine the road to the Channel ports was open to them. The trouble was, as usual, that Fritz was a little slow in his thinking, and he missed his chance. The Allies obtained time enough, by a miracle of industry on the part of British and French women, to make preparations, and then, after gas warfare was started, the Allies thought faster than the Germans, and finally beat them at their own game.

Now in regard to the "humanity" of gas warfare, it should be remembered that the American troops were originally not prepared against it. Our men were saved by the British. No fewer than 700,000 British gas masks were furnished to us before the American masks arrived. Our first gas officers and troops were trained by the British, and so well trained withal that they avoided accidents. It was only by means of this help that we may be said to have been partially ready. Despite this defect in preparation the following figures are illuminating. Of our total casualties in battle about 30 per cent arose from gas, leaving 70 per cent caused by all other forms of attack such as bullets, shrapnel, machine guns, high explosive shells, etc.

### GAS CAUSED ONLY 5 PER CENT OF DEATHS

But while the gas wounded equalled 30 per cent of our casualties, deaths from gas were only 5 per cent of the total deaths. In other words, of each 100 wounded with gas 3 to 4 die, while of each 100 wounded with bullets, high explosive, etc., 20 to 25 die. Deaths from pneumonia and other lung complications following gassing are included in the 3 to 4 per cent given. Of the total casualties from other causes, 20 to 25 per cent died, and this does not include the men who are maimed. We have more than 3000 men who have lost either a leg or an arm, not to count those who have been blinded. There is no authenticated case of permanent blindness from gas. The U. S. authorities in the very beginning prescribed the use of gas in all shells from 3 to 8 in. in diameter, and finally, last summer, the list was made to include all shells up to 9½ inches.

Against savages or semi-civilized tribes gas warfare may be made as humane as is desired. Lachrymator or tear gas will cause temporary

blindness so that enemy troops may be easily captured, though within a few hours the prisoners have their sight completely restored, and are not physically injured otherwise.

The training of gas troops is of primary importance. It is required of them that they use their noses to sniff out the first sign of gases. Sensitiveness to this grows as the men remain in the service. The men must know the hazards, and yet they must not be frightened so as to make them susceptible to panic. Protection must be adequate, but not a burden. Better a little hazard than discomfort which men cannot endure.

The entire system of defense needed to be changed with the advent of mustard (dichloroethylsulphide). Theretofore with chlorine, phosgene, diphosgene (trichlormethylchlorformate), etc., the attacks were intense but short lived. Mustard, however, which boils at about 217 deg. C., remains in place, and in cold, still weather lasts more than a week after it has been spilled upon the earth. This requires a more comfortable protection and the necessity of moving troops from gassed to free areas. Very fortunately this necessary change in tactics was synchronous with the change from trench warfare to an elastic front.

Gas troops also are drilled in the use of Livens projectors and bombs, and Stokes mortars, both of which are British contributions. The Livens projectors are 8-in. drawn steel tubes, either 2 ft. 9 in. or 48 in. in length. These are loaded with loosely fitting bombs 8 in. in diameter and about 14 in. long. They are fired simultaneously in groups of 50 to 2500. The Stokes mortar is a 4-in. heavy tube, by means of which 25 to 40 bombs, fitted with fuses to break them open, may be fired per minute.

#### NEED FOR CHEMISTS AS OFFICERS

Practice also shows the need of 3 to 5 chemical warfare officers on the staff of each commanding general to augment the artillery, as well as gas troops to follow up the infantry. It is also desirable that of the Chemical Warfare Division in the field, at least 25 to 30 per cent of the officers be sound chemists.

Laboratories are absolutely essential, and these must keep in close touch with the field. Leading authorities are of the opinion that the greatest hindrance to the work of the National Research Laboratory in Washington was its inability to keep in touch adequately with the fighting line. The vast number of reports which were lost, including thousands of pages of supremely valuable data which never arrived, made the situation worse. There were sent from France during the six months 360 reports, and of these a great many have not been found to this day. Defective communica-

tions were among our most expensive troubles.

Laboratories should be recognized as an intimate part of the fighting machine, inasmuch as only by this means can the constantly changing problems of this scientific method of warfare be met. The lack of enough and of very capably manned laboratories in chemical warfare is no less than an invitation to defeat. With proper laboratory co-operation, however, chemical warfare offers the greatest range for ingenuity to both officers and men in the field and on the staff.

On the other hand it is of signal importance that chemical warfare be under military guidance, because purely laboratory methods give wrong and harmful results. An instance of this may be cited in the case of vincennite, a French preparation of hydrocyanic acid which, while remarkably toxic upon dogs, was little more than useless in the field. The British succeeded earlier than the French in achieving active co-operation between their military and chemical staffs, and they benefited accordingly, contributed more, and made fewer errors. As soon as the French obtained this co-ordination their progress was immensely accelerated. Errors of the following type are typical of laboratory work without military communication and control; too tight elastics in masks, too long rubber mouthpieces, the wrong use of such a gas as vincennite, as stated above, etc.

The first American gas troops were trained by the British for three weeks. The first independent American gas attack was made along the front of the Rainbow Division in April, 1918, and so well did the troops acquit themselves that the regiment received the decoration of the Legion of Honor, and 26 Croix de Guerre were distributed among officers and men.

#### GAS TROOPS OF INCALCULABLE VALUE

As the art progressed it became part of every battle plan to answer the questions, "Where can we use gas?" and "Where can we use smoke?" Then as the battle proceeded the gas troops followed the infantry, and became machine-gun nests. The method came from the collaboration of various branches of the Chemical Warfare Service, wherein Stokes mortar bombs were employed, containing thermit and white phosphorus. They were remarkably effective. One single shot brought out 77 boches, hands up and crying "Kamerad!" This is but an incident of the ingenuity of the chemical division when it is well organized. Thermit has its faults; it cools very quickly, but the phosphorus gave it a bewildering quality. Whenever a smoke screen was needed the chemical troops were at hand to provide it. Against a massed attack a few bombs of phosgene and diphosgene were very



discouraging unless the men were adequately protected, for phosgene is quick in action and gives 20 per cent fatalities. It is, however, quickly dissipated. As the war neared its end our troops were able to protect themselves against a gas attack within fifteen seconds after the first flash.

#### SIZE OF AMERICAN CHEMICAL DIVISION

Another important service developed by the gas troops was the loading of Livens bombs filled with 30 lb. of TNT, of which they fired twenty or more at a time. As these bombs did not bury themselves in the earth they completely swept the area covered by them of every living thing. More than 1000 of these were made in the field in France and put over, and 2000 more were in the making. Here also screens of smoke were often followed by screens of gas. Again, the artillery would administer the doses while the chemical officers would select the medicine. So useful were these gas troops that by the spring of 1919 there would have been no fewer than 18,000 Americans in the chemical service abroad.

Not only the need of laboratories but the absolute necessity for them has been mentioned already. The Germans shot their first mustard in July, 1917, and the Allies came back with it eleven months later. Also in October, 1917, the development of the gas mask for long-time wear was begun. The final American type, which was by far the best one made, was a modification of the French Tissot mask, which permits breathing naturally through the nostrils, and in which the eye-pieces are kept clear.

Another result of the research laboratory while under Colonel Bacon was the discovery that boiled linseed oil had a marked influence in retarding mustard burns. Further research brought out the fact that this was due to metallic salts dissolved in it. It resulted in what was called "sag paste," a mixture of zinc stearate and vegetable oil, about half and half, which made an effective unguent. It did not prevent burns, but it took about six times the concentration necessary to cause burns without it.

#### CAMOUFLAGE GASES PREPARED

Camouflage gases were prepared to disconcert the enemy smellers. These were nearing completion at the time of the armistice. They made it impossible for Fritz to know what he was getting.

Other contributions in research were a saving of from one to two million dollars in specifications for camouflage paints, a fire extinguisher for aeroplanes, a new aeroplane glue, analyses of gases from German shells, the testing of masks, fabrics and smoke canisters or boxes attached to masks, because, while or-

ders were given for each man to record the time he used his mask in gassed area, it did not work in practice. The men would not keep the records as prescribed while they were busy fighting.

Research both at home and in England resulted in technology superior to that of the Germans; indeed, toward the end of the war, the Germans' leading spy was operating in France and elsewhere to discover how mustard could be made in such quantity. The Germans at no time were able to produce over six tons of it daily. This superiority was evident as early as 1917, when rumors were rife that a German professor of humane tendencies was urging upon the International Red Cross the need of coming to a conclusion with the war, on the ground that by the spring of 1918 the Germans would launch such a fatal poison that it would produce nothing less than a holocaust among the Allies. It was suspected that this was an exponent of German fear rather than of German humanity, so word was sent back that the Allies hadn't really begun to fight with gas yet, and had no thought of quitting.

#### TROUBLES IN ESTABLISHING CHEMICAL WARFARE

As for the troubles which had to be met in establishing chemical warfare their name was legion. The first requirement was personnel, and there wasn't any. "State your requirements," said headquarters, and nobody knew what they were. Personnel was, however, finally assembled, and among the splendid corps of men the following are worthy of special mention:

Colonel E. J. Atkinson (West Point '08), of the First Gas Regiment, which went over as the Thirtieth Engineers.

Colonel Richmond Mayo Smith (of Plimpton Press, Norwood, Mass., and N. Y.), in charge of supplies.

Lieutenant-Colonel Byron C. Goss, in charge of gas warfare at the front, a wonderful instructor in the subject.

Colonel G. N. Lewis (University of California), whose military sense was equal to his quick and profound chemical understanding.

Major Carl Connell (New York University), who developed the final type of mask.

Major Zanetti (Columbia University), chief liaison officer, with the French.

Major Joel H. Hildebrand (Professor at University of California), in charge of experimental field and officers' gas school.

Colonel Raymond M. Bacon (Director of Mellon Institute), in charge of research.

Major Keyes (Boston Tech), in charge of research laboratory in Paris.

Captain Boothby, who taught mask drill.

And many others.

There was also Colonel Harrison of the British Army, who was a tower of strength in getting gas masks from England to our men, by cutting red tape and coming to the rescue. He was engaged in pharmaceutical chemistry in London, enlisted as a private at the age of 46, and died last year as a Brigadier General.

It took two months from the time munitions left the United States to reach the army at the front. While this was not always the case, it was necessary to count upon such a lapse of time. And communications, so far as forwarding reports, etc., were concerned, were no less than desperate.

#### GAS INVITING FOR POLICE WORK, BECAUSE EFFECTIVE WITHOUT INVOLVING FATALITIES

In conclusion, while conventions may agree to forbid the practice of chemical warfare, it is, as we have said, a remarkable weapon of offense. Its employment places an army at so

great an advantage over an unprepared enemy that it will be difficult to trust nations to forego its use. It is exceedingly inviting for police work, because it may be made effective without involving fatal casualties or maiming. The question, therefore, must be met whether future wars shall be controlled or not. If they are to be fought under international supervision, under rules akin to an international code duello—in which event it would seem that swords alone should be the proper weapon—then we have every reason to hope for the best, so long as the supervisors do not get to fighting among themselves. On the other hand, it may be that scientific warfare will be recognized, and allowed to develop until war itself shall be prohibited by some working agreement owing to its destruction of the world's accumulated property. Half-way measures and compromises will not meet the situation. And if there is to be an international police then chemical munitions will be needed to avoid unnecessary loss of life.

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## Electrolytic Production of Hydrogen

BY HARRY L. BARNITZ, PH.G.

THE decomposition of water into its constituent elements, hydrogen and oxygen, had been a matter of experiment in the chemical laboratories for more than a century. It finally remained for the remarkable developments of electrochemistry in the past generation, stimulated by the commercial demand for these gases, to produce a commercially practical water electrolyzer (also termed electrolytic cell).

In an embryonic form, decomposition of water may be effected by passing an electric current between two metallic poles, or electrodes, immersed in water. As water has great power of resistance to electric current, it is necessary to lower the resistance to allow a large current of electricity to pass. This is accomplished by adding to the water either acid or alkali, forming an electrolyte. The electrolyte proportionally raises the gas production.

There are two classes of substances which act as conductors for the electric current. The first class includes metallic conductors, such as copper, aluminum, brass, iron, mercury and some solid non-metallic substances, of which carbon is the most important. The passage of a current through these conductors is not accompanied by any change in the conductor, other than the development of a certain

amount of heat. Members of the second class of conductors known as electrolytes are water solutions of acids, bases and salts. Some melted compounds also act as electrolytes—these will not be considered here, as they are of no importance in the production of hydrogen and oxygen.

The passage of current through an electrolyte is accompanied by the liberation of two different substances. One of these appears at the terminal where the current enters the solution, known as the anode, or + electrode, and the other at the terminal at which the current leaves, called the cathode, or — electrode. For an illustration, if two electrodes made of platinum plates are placed in a strong aqueous solution of hydrochloric acid, the one electrode being connected to the positive pole of the battery and the other to the negative pole, decomposition of the liquid will take place—hydrogen will be given off at the negative electrode or cathode and chlorine at the positive anode. If the solution of hydrochloric acid is replaced by sodium chloride, chlorine is liberated at the anode and sodium hydroxide is found in the solution surrounding the cathode.

Now let the solution of hydrochloric acid and sodium chloride be replaced by a solution of sodium hydroxide. The solution of sodium hydroxide is split up by the current into oxy-

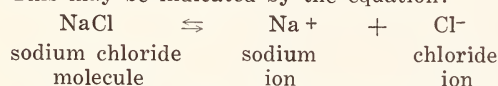


gen, which is liberated at the anode, and sodium ions, which lose their charge at the cathode and become sodium atoms with the escape of hydrogen. Again, the solutions of hydrochloric acid and sodium chloride and sodium hydroxide are replaced by an aqueous solution of sulphuric acid. In this instance, hydrogen will be liberated at the cathode and the  $\text{SO}_4$  group at the anode, which immediately reacts with the water and forms a new molecule of sulphuric acid.

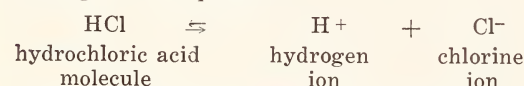
#### ELECTROLYTIC DISSOCIATION THEORY

Before attempting to explain this result it will be necessary to state the theory of electrolytic dissociation.

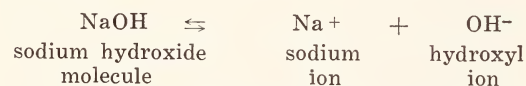
According to this theory, when an electrolyte is dissolved in water, a portion at least of its molecules break up into two parts, one charged with positive electricity and the other with an equal amount of negative electricity. These charged portions of the molecule are called respectively positive and negative ions. Thus, when sodium chloride is dissolved in water, equal amounts of positive sodium ions and of negative chlorine ions are produced. This may be indicated by the equation:



Hydrochloric acid dissociates in solution according to the equation:

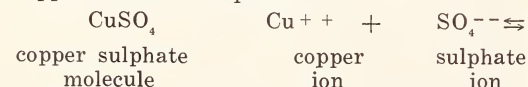


Sodium hydroxide dissociates in solution as follows:



It will be noted in these typical examples of the dissociation of a salt, an acid, and a base that the hydrogen ion and the metallic ion are positive, and that the non-metallic ions are negative.

In a solution of copper sulphate there are copper ions and sulphate ions:

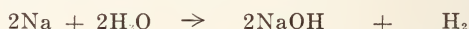


A double charge is indicated here on each ion, as the number of charges which an ion carries is the same as the number expressing its valence. Molecules of the dissolved substance in an electrolyte, then, dissociate, on dissolving, into positive metallic ions and negative non-metallic ions. Hydrogen, in acids and acid salts, acts as a metallic ion; in bases it is a part of the complex non-metallic ion

$\text{OH}^-$ . The only important complex positive ion is  $\text{NH}_4^+$ , produced by the dissociation of ammonium hydroxide and the ammonium salts.

The proportion of the molecules dissociated at a particular time in a given electrolyte depends on the nature of the dissolved substance, the degree of dilution of the solution, and the temperature. Water is the only important solvent in which any considerable amount of dissociation takes place. Many soluble substances, particularly organic compounds such as sugar, alcohol, and glycerine, do not dissociate on dissolving. Such solutions are known as non-electrolytes and are non-conductors of electricity. Pure water is a very poor conductor, and therefore its molecules are only slightly dissociated.

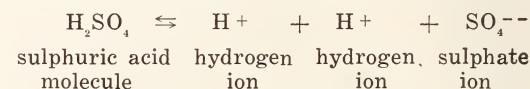
On the basis of the theory just stated the electrolysis of sodium chloride is easily explained. When the electrodes are dipped into the solution and the circuit closed, the  $\text{Na}^+$  ions, which have been moving about at random in the solution, are immediately repelled by the positive electrode and attracted by the negative electrode, since like electric charges always repel and unlike charges attract. The  $\text{Cl}^-$  ions begin to move forward toward the positive electrode for the same reason. As soon as an ion reaches the electrode, the opposite charges on ion and electrode neutralize each other. The chlorine ion, losing its charge, becomes a chlorine atom; these unite in pairs to form molecules, and escape from the solution, when a sufficiently large number of such molecules have collected at the anode. The sodium ions in a similar way lose their charge at the cathode and become sodium atoms. These do not, however, unite to form pieces of metallic sodium, since they react with the water to form sodium hydroxide:



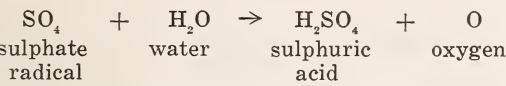
sodium water sodium hydroxide hydrogen

Thus bubbles of hydrogen will escape at the cathode. The sodium ion did not react with the water, because the presence of the electric charge gives the ion chemical properties differing from those of the atom.

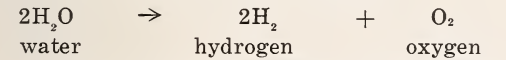
It may be now explained that when sulphuric acid is added to water to make it a conductor (considering the action first as an electrolysis of sulphuric acid) the acid dissociates on dissolving into hydrogen ions and sulphate ions:



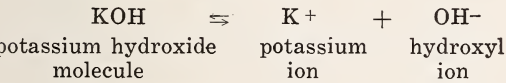
As the current passes, the ions lose their charges at the electrodes. At the cathode hydrogen ions change to hydrogen atoms, which unite to form molecules of hydrogen. At the anode,  $\text{SO}_4^{--}$  changes to  $\text{SO}_4$ , which immediately reacts with the water as follows:



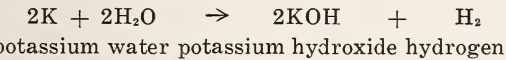
In the reaction a new molecule of sulphuric acid has been produced in place of the one originally dissociated and an atom of oxygen has been liberated. The oxygen atoms liberated at the anode unite to form oxygen molecules, which escape as a gas. The entire reaction therefore may be considered as equivalent to that shown by the equation:



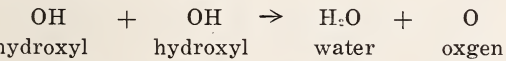
In the commercial production of hydrogen and oxygen by electrolysis where a solution of sodium hydroxide or potassium hydroxide is used as the electrolyte, potassium hydroxide has a slightly higher efficiency than sodium hydroxide and was almost exclusively used prior to the war. Due to the high cost and great scarcity caused by the war, potassium hydroxide has been replaced by sodium hydroxide, although it is probable that potassium hydroxide will again be used when market conditions are favorable. The first action in the electrolysis is the dissociation of potassium hydroxide when it dissolves:



When the potassium ion reaches the negative electrode, it loses its charge, becomes a potassium atom, and reacts with the water of the solution, forming potassium hydroxide again and liberating hydrogen:



The hydroxyl ions, when they lose their charges, react with each other, forming water and liberating oxygen:



It will be seen that the net result of these reactions is the removal of one molecule of water from the solution and the liberation of two atoms of hydrogen and one atom of oxygen. So it is only the water in the cell which needs to be renewed and not the potassium hydroxide. The results of the reaction are identical if sodium hydroxide is used as the electrolyte.

FARADAY'S LAWS

The dissociation theory having been stated, the theory of relationship between current and volume of hydrogen produced will now be considered.

The theory of relationship between current and volume of hydrogen produced is founded upon laws relating to the decomposition of

liquids by the electric current, known as Faraday's laws. They constitute the basis of all electrochemical calculations, determining just how much chemical action is produced by a given flow of current for a given time. These laws are as follows:

1. The amount of chemical effect produced during electrolysis is directly proportional to the product of the current and the time; that is, to the quantity of electricity which flows through the electrolyte.

2. When a current passes through an electrolyte, bringing about chemical changes at the electrodes, the quantity of each substance formed is directly proportional to the equivalent weight of the substance and to the quantity of electricity which has flowed through the electrolyte.

It is obvious that if 1 amp. flowing for 1 min. will deposit a certain amount of silver, 2 amp. flowing for 1 min. will deposit twice that amount. Also that the amount which a given current will deposit in 10 min. is ten times as great as will be deposited by the same current in 1 min.

ELECTROCHEMICAL EQUIVALENT

By knowing the equivalent weight, or, as it is more commonly termed, the chemical equivalent, of the material, the quantity of that material which will be liberated by a known amount of electric current can be readily calculated. Every substance, whether it be a chemical element or a chemical compound, has its electrochemical equivalent, just as it has a certain atomic weight; and in fact the electrochemical equivalent is closely associated with the atomic weight. As many elements have more than one valency, therefore they have more than one chemical equivalent weight, as can be seen from the Table I.

TABLE I. CHEMICAL EQUIVALENT WEIGHTS			
Element	Atomic Weight	Valency	Chem. Equiv. Wt.
			at wt.
Hydrogen.....	1	1	1
Oxygen.....	16	2	8
Gold.....	197	3 or 1	65.6 or 197
Tin.....	118	4 or 2	29.5 or 59
Tungsten.....	184	6 or 4	30.6 or 46.0

It is found by experiment that a current of 1 amp. flowing for 1 sec. (one coulomb) deposits 0.001118 g. of silver from an aqueous solution of a silver salt. The atomic weight of silver is 107.94, its valency is unity, therefore its chemical equivalent weight is 107.94. However, the atomic weight of hydrogen is 1.0 and its valency is unity, therefore its chemical equivalent weight is 1.0; therefore it is obvious from Faraday's second law that  $\frac{0.001118}{107.94}$ .



= 0.000010357 g. of hydrogen will be liberated by 1 amp. flowing for 1 sec., or the mass of hydrogen liberated by any current in any time may be expressed as  $1.0357 \times 10^{-5} At$ , where  $A$  is the current in amperes and  $t$  the time it flows in seconds; which is equivalent to stating that, at 0 deg. C and 760 mm. barometric pressure (29.92 in.) 1 amp.-hr. will liberate 0.0147 cu.ft. of hydrogen.

#### FACTORS AFFECTING VOLTAGE DROP

It now remains to determine the relationship between power and the volume of hydrogen which should be theoretically liberated. It is evident that to get the current to flow through the electrolyte requires an electrical pressure, as all substances offer resistance to the passage of electricity through them. Therefore a voltage drop between the anode and cathode will be found in cells.

Two factors of resistance cause this voltage drop, one of which is analogous to the resistance of any conductor and is dependent on the length and cross-sectional area of the path of flow of the current—the distance between the electrodes. This resistance is called the back emf. of the cell, or polarization. The resistance in the first instance can be practically eliminated by placing the electrodes close together. The second factor is due to a constant of the electrolyte in the cell and is not caused by a function of cell design. Therefore it is obvious that the current must have a certain theoretical potential to overcome the polarization resistance of the electrolyte to obtain electrolysis in a cell.

Decomposition voltages are given in Table II for various aqueous solutions of bases, acids, and salts containing their chemical equivalent weight in grams per liter. These values are given for minimum voltage to produce continuous electrolysis in a cell whose resistance other than that due to polarization is negligible. These solutions vary in concentration, and it has been found that solutions whose minimum voltage is about 1.7 require no appreciable variation of pressure to produce continuous electrolysis.

Having previously ascertained, from Faraday's laws, that a current of 1 amp. for 1 hr. should produce 0.0147 cu.ft. of hydrogen (at 0 deg. C. and 760 mm. pressure), it is evident when a solution of sodium hydroxide is used, the current must be supplied at 1.69 volts, therefore  $1 \times 1.69$  watt-hr. produces 0.0147 cu.ft. of hydrogen, or 1,000 watt-hr. produce  $\frac{0.0147 \times 1000}{1.69} = 8.7$  cubic ft.

With the liberation of hydrogen at the cathode, oxygen is simultaneously evolved at the anode. Therefore, in accordance with Faraday's laws the volume of oxygen is one-

TABLE II. DECOMPOSITION VOLTAGES  
(Le Blanc)

Solution of	Minimum Voltage Volts	Solution of	Minimum Voltage Volts
Silver nitrate.....	0.70	Nitric acid.....	1.69
Hydrochloric acid.....	1.31	Zinc chloride.....	1.78
Potassium hydroxide...	1.67	Zinc sulphate.....	2.35
Sodium hydroxide.....	1.69		

half of that of the hydrogen and theoretically, in the electrolysis of a solution of sodium hydroxide, 1 kw.-hr. should produce 8.7 cu.ft. of hydrogen and 4.4 cu.ft. of oxygen at 0 deg. C. and 760 mm. (29.92 in.).

One of several of the more important commercial applications of the theory of electrolysis will now be described in the production of hydrogen and oxygen.

#### TYPES OF COMMERCIAL CELLS

Various types of electrolytic cells for the commercial production of hydrogen and oxygen have been developed. Only those types which are representative will be considered here. They all employ either sulphuric acid or a solution of sodium or potassium hydroxide as electrolyte. When the acid is used, lead is the material used in the cell construction, while with the alkaline electrolyte, iron is employed. This choice of materials is made because of the insolubility of lead and of iron in the respective solutions. It is apparent that insoluble electrodes must be employed to allow the escape of hydrogen and oxygen.

An important point to be attained in water decomposition is that the anode and cathode products be kept as completely separated as possible. The bubbles of the hydrogen coming off at the cathode surface must not mingle with the oxygen bubbles from the neighboring surface, otherwise impurity of products results.

The electrodes must be placed as near together as practicable. If the distance between the anode and cathode is great, the resistance of the cell is high and the production is much below the theoretical.

To obtain reasonably high purity in the gaseous products, some types of cells have a porous diaphragm placed between the electrodes; others have a metallic diaphragm. Cells employing a porous diaphragm create a certain amount of resistance, but they have the advantage of acting as a factor of safety and add to compactness.

A 20 to 30 per cent sulphuric acid solution has a higher conductivity than a 10 to 20 per cent alkali solution. On the other hand, it takes a somewhat higher electromotive force to liberate hydrogen and oxygen from the former solution, so that cells using sodium or potassium hydroxide have a slightly lower

energy consumption than those using the acid. Since the acid or alkali is unaffected by the electrolysis, it is only necessary to add distilled water from time to time to replace that electrolyzed.

The representative types of cells for the commercial production of hydrogen may be classed as:

- 1. Metal diaphragm type.
- 2. Filter press or bi-polar type.
- 3. Suspended diaphragm tank type.
- 4. Non-porous non-conducting diaphragm type.

METAL DIAPHRAGM TYPE

The cell developed by Garuti and Pompili<sup>1</sup> is an excellent example of this type. In this cell a partition of iron separates the anode

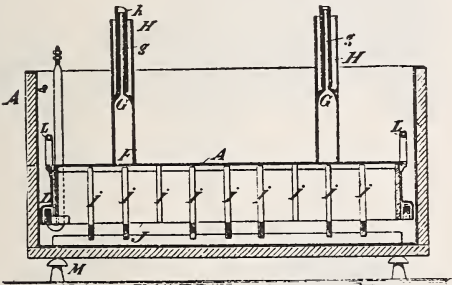


FIG. 1. GARUTI GENERATOR—VERTICAL LONGITUDINAL SECTION

from the cathode, and this partition is prevented from becoming an intermediate electrode by keeping the voltage applied to the cell too low for this to take place. The current flows from the anode to the cathode around the bottom of the iron partition.

Fig. 1 is a diagrammatic longitudinal verti-

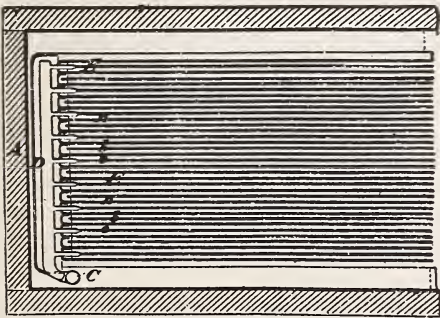


FIG. 2. GARUTI GENERATOR—HORIZONTAL SECTION

cal section through the center, Fig. 2 is a horizontal section of one end, Fig. 3 is a verti-

cal cross-section of the cell and Fig. 4 a plan view of conductors and electrodes.

Tank A of wood lined with iron a contains the electrolyzer, which consists of an inverted tank A which is divided into cells E by longitudinal diaphragms. This case is made of iron and is open only at the bottom. The anodes b and cathodes c are placed one in each cell, taking care that each anode is between two cathodes. The gas passes through an opening at the top of each chamber into the gasometer containing the same gas. The electrodes are insulated from the diaphragms by combs I made of wood, the teeth of which enter the cells and fill the spaces between the electrodes and diaphragms. L is a handle for lifting out the electrolyzer.

The diaphragms may be perforated near the bottom with a large number of small holes, which reduce the electrical resistance, as there

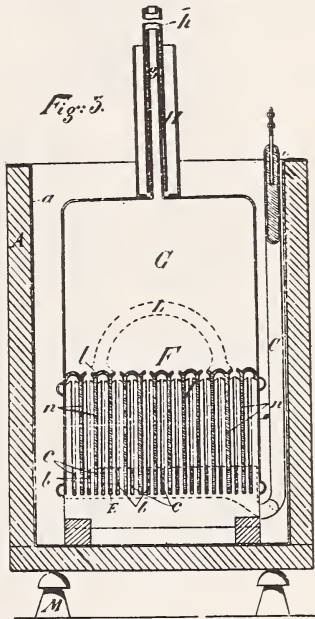


FIG. 3. GARUTI GENERATOR—VERTICAL CROSS-SECTION

is very little danger of the gases becoming mixed at this point.

Using a 25 per cent solution of sodium hydroxide and a current density of 25 to 27 amp. per sq.ft., the gases being measured at 20 deg. C. and 760 mm. pressure, the electrolyzer produces 6.1 cu.ft. of hydrogen per kw.-hr. The purity of the hydrogen is 99 per cent and of the oxygen 97 per cent. This type of cell is quite compact but, owing to the small distance between the electrodes, care must be taken to prevent an internal short circuit in the individual cells.

<sup>1</sup>U. S. Patent 629,070, July 18, 1899.



### FILTER PRESS OR BI-POLAR TYPE

In the filter press or bi-polar type cell the polarization or back emf. resistance of the cell from the original anode to the original cathode is doubled by the fact that the interposition of a conductor, to which no electrical connections have been made, turns the original cell into two cells, when the electrodes are placed together and insulated from one another.

The filter press or bi-polar type shown in Fig. 5 consists of a series of metallic plates (electrodes) clamped up together in a heavy frame, electrically insulated from one another, and separated by diaphragms of porous fabric.<sup>2</sup> Each pair of these electrodes

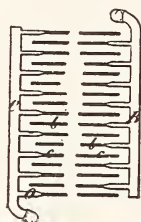


FIG. 4. GARUTI GENERATOR—PLAN VIEW OF CONDUCTORS AND ELECTRODES

forms a closed cell, divided by the diaphragm. These cells are filled with the electrolyte (sodium or potassium hydroxide), which acts as a conductor, connecting up the plates in series.

An electric current admitted at one end plate passes on through the plates and through the solution to the other end plate. In its passage, it decomposes the water of the solution into the two gases—hydrogen and oxygen—which are released on opposite sides of each plate and emerge upward into the gas oftakes. The mingling of the hydrogen and oxygen in each cell or compartment is prevented by the diaphragm which, while permitting the passage of the fluid, resists the passage of the gases.

The electrodes *C* are clamped together by a heavy screw *D* working in the rear support. The surfaces of the electrodes carry vertical corrugations which are interrupted by a large number of depressions to facilitate the flow of electrolyte into the cell and the release of the gases from it.

At top and bottom of each electrode are two openings communicating by cored channels with opposite sides of the plate. Those at the bottom are for the water intakes and those at the top are for the gas oftakes. It will be seen that each half has its own independent water intake and gas outlet, so that there can be no possibility of the two gases mingling through these channels.

The diaphragms *H* are of specially prepared asbestos fabric. All around the edge of this fabric is molded a packing rim *G* of pure rubber which is an integral part of the diaphragm and which rests in a recessed groove on the face of the electrode.

Obviously, in a generator of this type, an essential of power economy is that all the current supplied shall pass through the electrolyte and none of it be bypassed through the metal of the generator or through the water inlets and gas outlets, therefore the electrodes are insulated from the side bars of the frames

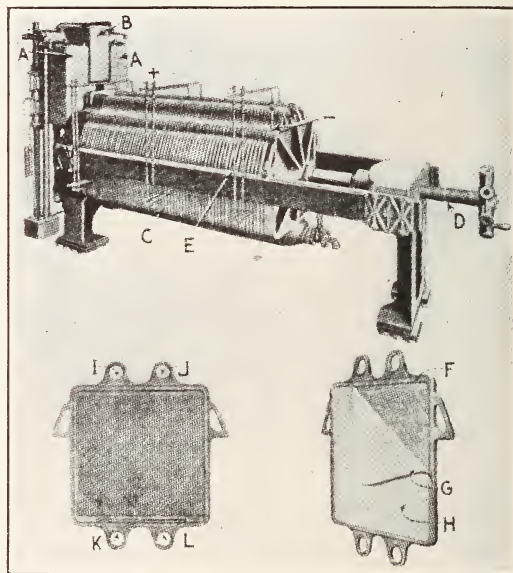


FIG. 5. FILTER PRESS OR BI-POLAR TYPE CELL

Above—Cell completely assembled. Lower left—Electrode from anode side, showing water intake and gas oftake channels and corrugations. Lower right—Electrode with diaphragm partly removed, showing method of holding and packing the diaphragm.

by porcelain insulators *E* resting on a wooden base. They are insulated from one another by the rubber packing rim *G* surrounding the diaphragm and by rubber nipples inserted in the water intake and gas oftake shoulders of the electrodes, which also provide an insulating tube in the interior of the water intake and gas oftakes.

At the front of the cells and elevated above the electrodes is a solution box or tank *B* which receives the distilled water that is supplied to the electrode chambers or cells *C*. From this tank a pipe descends to a water-feed manifold, the latter branching to two independent connections to the two separate water intakes to the cells. And from this

<sup>2</sup>MET. & CHEM. ENG., vol. 14, p. 108, Jan. 15, 1916.

manifold two risers lead, one to each of the two gas domes *AA* shown in Fig. 5.

Into these gas domes the hydrogen and oxygen are separately introduced as generated. The arrangement is such that a constant fluid level between the electrodes is automatically maintained. The description will apply to all filter press type cells.

As the individual resistances are in series, the number of plates in the unit determines the actual voltage necessary. The voltage drop per plate is 2.4 to 2.5 when using a 28.9 per cent solution of sodium hydroxide. The aver-

of the tank *G* and also the metal partition *M*. The asbestos sack is held by a fixture band *J* on the non-conducting separator *I*.

Either one or two diaphragms may be used in this type cell. In the diagrammatic sketch a partial view of one diaphragm is seen with a partition of mild sheet steel *M* which separates the other diaphragm (not seen in the sketch).

The lid *O* is insulated and bolted down on the flanged top of the tank. To this lid is attached the filling cup *E*, gas outlet pipes *A* and *B* and positive busbar *F*. The negative busbar *P* is attached to the side of the tank and extends above the lid.

The interior of the tank is filled to within about 10 in. of the cover with a 15 per cent solution of sodium hydroxide in distilled water.

The mode of operation of the cell is as follows: If the positive lead of the circuit is connected to busbar *F*, and the negative lead is

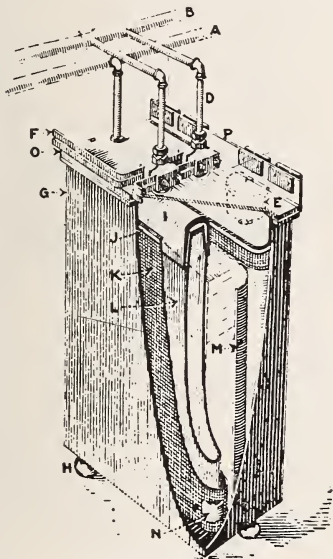


FIG. 6. SUSPENDED DIAPHRAGM TANK TYPE CELL

age current density is about 20 to 30 amp. per sq.ft. and the production is 7.5 cu.ft. of hydrogen and 3.75 cu.ft. of oxygen per kw.-hr. measured at 20 deg. C. and 760 mm. pressure. The purity of the gases averages between 99.1 and 99.5 per cent for the hydrogen and 98.7 per cent for the oxygen.

The filter press type of cell is compact, but is offset by other disadvantages. Water and gas tightness in the individual cell depends upon the rubber in the diaphragms and on contraction and expansion. This type of cell requires constant overhauling. The suspended diaphragm tank type cell, as illustrated by the diagrammatic drawing (Fig. 6), consists of an oblong tank *G* made of mild sheet steel with flanges at the top standing on insulators *H*. In this tank an oblong diaphragm with curved ends and bottom *L*, perforated with oblong holes, is suspended from the thick steel lid of the cell *O*, by means of hollow electrodes *D*. An asbestos sack *K* surrounds the diaphragm *L*, which forms a partition between the side

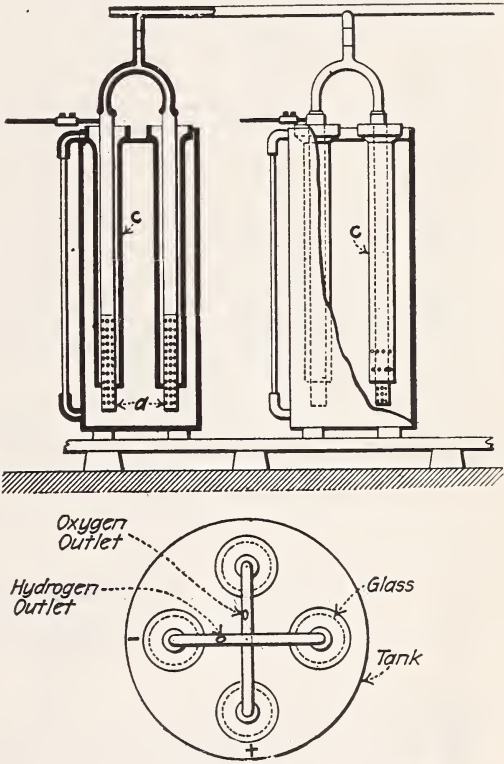


FIG. 7. SCHOOP ELECTROLYZER

connected to busbar *P*, electrolysis will take place and hydrogen will be liberated on the side of the tank *G*, rising through the electrolyte, where it is free to circulate to the outlet pipe *A*. While hydrogen is being liberated on the sides of the tank *G* and partition



*M* oxygen will be liberated on both sides of the diaphragm *L*, from where it will rise up and pass out of pipe *DD*. In each of the four corners of the asbestos sack is a pocket *N*, which holds an insulator which permits on the outside diaphragm *L* the free circulation of oxygen bubbles by expanding the sack slightly. Distilled water is added to the filling cup *E* from time to time, to replace that decomposed by the current. The voltage drop between anode and cathode is 2.2 volts. The purity of hydrogen is above 99½ per cent and that of the oxygen above 99 per cent. The suspended diaphragm tank cell has been one of the most successful types of cell developed.

An example of the non-porous non-conducting diaphragm type is represented in the Schoop cell (Fig. 7) in which an acid electrolyte is used. The electrolyzer consists of a cylindrical lead-lined tank containing four vertical electrodes. These are in the form of lead tubes filled with fine lead wire to increase active electrode surface. Each electrode is surrounded by a cylindrical tube of glass or porcelain—open below and perforated at the bottom to allow the flow of current. The gas generated on the electrode within the glass or porcelain tube passes upward, where it is collected. Where an alkaline solution is employed the tank and electrodes are made of iron.

#### HYDROGEN AS BYPRODUCT FROM ELECTROLYTIC CHLORINE CELLS

Some electrolytic cells designed for the manufacture of products other than those already discussed yield hydrogen as a byproduct, i.e., those used in the electrolytic process for the manufacture of caustic-soda.

The Castner mercury cell (Fig. 8) is probably the most important type of cell yielding hydrogen as a byproduct. The function of this cell is primarily the production of caustic

soda and chlorine from a solution of brine, but at the same time hydrogen is produced.

The cell is divided into three compartments by vertical partitions extending almost to the bottom of the cell, but not making a tight joint therewith. In the two end compartments *A* and *C* is placed a strong solution of brine, while the middle compartment *B* is filled with water. The current, in flowing through the cell, passes from the positive carbon *DD* through the brine, thence to the mercury and from the mercury to the negative electrode *E* in the center compartment. By the splitting up of the sodium chloride in the end compartments, chlorine will be liberated at the posi-

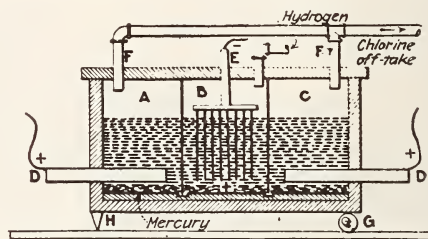


FIG. 8. CASTNER CAUSTIC SODA-CHLORINE CELL

tive electrode and passes out at *F*, while sodium will be deposited on the mercury, forming sodium mercury amalgam.

This amalgam is transferred to the central compartment by a slow rocking motion which is given the cell by the eccentric *G* and is decomposed at the negative electrode in accordance with the following equation:



It will be seen that the net results of the process are that chlorine is produced in the end compartment, and caustic soda and hydrogen in *B*, the center one. The hydrogen usually contains a certain percentage of chlorine which is detrimental.

## Furnace for Testing Firebrick Under Load at High Temperatures

BY C. H. LOVEJOY

THE proposed standard test for firebrick under load at high temperatures, outlined in the 1918 *Proceedings* of the American Society for Testing Materials, and more extensively described in this journal of date Jan. 1, 1918,<sup>1</sup> leads me to write this description of a furnace for similar purpose, which has been

used by the Pittsburgh Testing Laboratory, Pittsburgh, Pa., for the past five years. The main differences between these furnaces lie in the manner of applying the load and the means of determining the load at any time during the progressive failure of the brick under test.

The apparatus consists essentially of a firebrick chamber in which the test brick is heated while a pressure is applied at the ends.

<sup>1</sup>"A Furnace for Testing Refractory Materials Under Load at High Temperatures," Robert J. Montgomery, *MET & CHEM. ENG.*, vol. 18, No. 1, p. 18, Jan. 1, 1918.

We use a pressure of 50 lb. per sq.in. (double that recommended), which will produce ultimate failure in all but the best brick when the temperatures mentioned in the proposed test are attained. By applying the load with a spring instead of levers, we are able to carry practically all our tests to ultimate failure, determine the variation in load sustained by the brick at the higher temperatures, and obtain an idea of the rate of failure. The spring we use is easily removed and frequently checked up in our testing machine. This is mostly a matter of form, for when in use it is never stressed to capacity, and we have found no appreciable differences in it during the five years it has been in service. When compiling our results we plot a load-temperature curve as well as a time-temperature curve. As a rule we try to have our time-temperature curves alike and draw our conclusions from the load-temperature curve.

The apparatus is best described by outlining the procedure followed in making a test. The brick to be tested, *T*, is placed in the center of the furnace (Fig. 1); the upper end blocked to the roof with half of a refractory brick, the lower end blocked to the moving piston, *P*, with another refractory brick. To guard against eccentricity in loading, a very thin piece of sheet asbestos is placed between the blocks. The opening in the bottom of the furnace is closed by a piece of heavy asbestos board fitted around the lower blocking brick. The piston *P* is raised by turning nut *N* until the brick to be tested and the blocking are in firm contact with each other. The length of the uncompressed spring is now

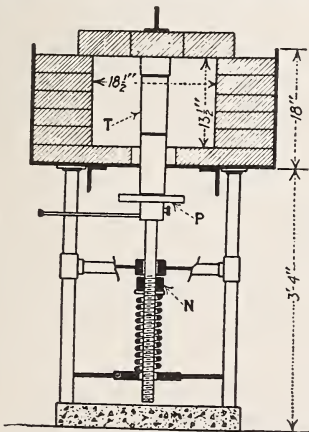


FIG. 1. SECTION THROUGH FURNACE

measured accurately. Further turning of nut *N* will produce compression in the spring and bring pressure to bear on the end of our test brick. For each inch of compression in the spring we use, we obtain 400 lb. load. Sup-

pose the end area of our brick to be 2 1/4 in. x 4 1/4 in. = 9.56 sq.in. at 50 lb. per sq.in. = 478 lb. total load to be applied. This will be obtained by continuing to turn nut *N* until the spring is compressed  $478 \div 400 = 1.19$  in. The two gas burners at *B* and *B* (Fig. 2) are lighted, at first without any air blast. These burners are staggered so that no flame shall impinge upon the test specimen. When the furnace has reached 500 deg. C. the door *D* is blocked, the blast turned on, and regu-

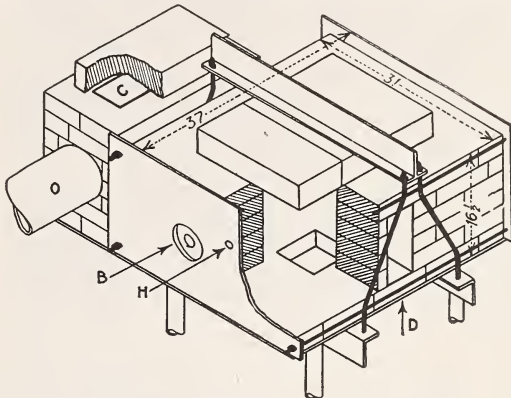


FIG. 2. ISOMETRIC VIEW OF HEATING CHAMBER

lated so as to reach 1350 deg. C. in five hours, and maintained at this temperature for one hour. Furnace temperatures are read every 20 minutes by an electric pyrometer inserted through *H*, opposite the brick. The amount of compression in the loading spring is measured at the same time. Very poor brick will start to fail and bulge in the middle as low as 950 deg. C. or 1000 deg. C., the load

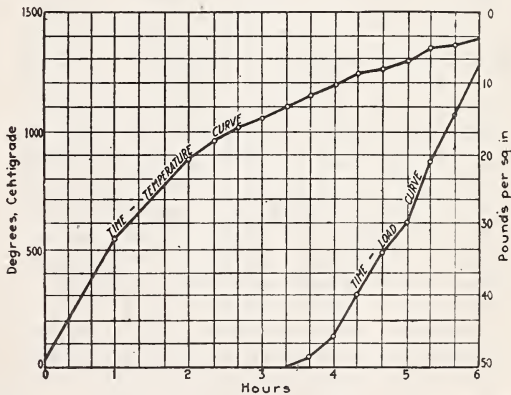


FIG. 3. TEST OF FAIR QUALITY FIREBRICK

falling off in proportion as this deformation reduces the amount of compression in the spring. Such brick will show complete failure below 1200 deg. C., the spring having returned to its original length, the load reduced to zero.



This class of brick is not useful in arch construction or other work where it is necessary that the brick stand a load. Fair brick will start about 1100 deg. C. and still have about 25 lb. per sq.in. left on them at 1350 deg. C. First-class brick will generally show no signs of failure before 1200 deg. C. and many will stand 1300 deg. C. before starting to fail. We have found only two brick that would show no signs of failure at 1350 deg. C. If desired the temperatures may be carried above 1350 deg. C. to whatever point is necessary to produce complete failure; always at temperatures below 1500 deg. C.

Considerable difficulty was experienced with the original furnace through the frequent melting off of the outlet pipe carrying away the gases, until the extra chamber C was built on the rear of the furnace.

In the proposed standard test using the lever furnace, the load remains constant, and different rates of heating are recommended for different qualities of brick, always stopping short of ultimate failure. In our work we re-

ceive samples from many sources in which the main question is not what this specimen will stand without failing but what this brick is good for and where it will fail. Our furnace enables us to arrive more quickly at the answer to this question.

For general testing and variety of service we have found this furnace very satisfactory. The metal work is simple and easy to assemble; the spring insures straight line application of the load; the brick work is made without special shapes and is easily laid up; and the whole furnace is compact and was moved twice in the last year with a minimum of effort.

The credit for the general design of this furnace belongs to J. B. Shaw, who built the original furnace. Several attachments have been added by other members of our staff for the purpose of making it automatic and self-recording, but it is not essential to describe them here.

Pittsburgh Testing Laboratory,  
Pittsburgh, Pa.

## The Absorption of Gases in Spray Systems and Towers

BY EDWIN M. BAKER

IN PROBLEMS involving the absorption of a gas by a liquid it is generally desired to absorb or dissolve some one constituent of a gas mixture by the liquid. It will be found convenient to call the gas to be absorbed or dissolved simply the "gas," and the gas mixture containing this gas and other diluting gases the "gas mixture." The absorption of gases in liquids may be divided into three subdivisions of a general class, in which most absorption problems will fall. First, the case where the nature of the gas and liquid is such that a chemical reaction takes place so that the gas will not exert any appreciable vapor pressure after absorption. The absorption of ammonia gas in an excess of sulphuric acid would be an example. Second, the case where the nature of the gas and liquid is such that a chemical reaction takes place, but the compound formed is sufficiently unstable so that the dissolved gas exerts an appreciable vapor pressure. The absorption of ammonia gas in water would be an example. Third, the case where no chemical reaction takes place between the gas and liquid, and where the liquid exerts a vapor pressure directly dependent on the amount of absorbed gas. An example of this is the absorption of the so-called gasoline content of natural gas in heavy mineral oil. Different combinations of gases and liquids may be found which will

give a series of conditions gradually shading from the first to the third subdivision. In this general class, then, are included the cases where simple or no chemical reactions take place. It does not include complicated reactions such as take place on the introduction of oxides of nitrogen with excess oxygen in the form of air into absorption towers; where water is used as the absorbing agent to form nitric acid; and where the oxidizing of the lower oxides of nitrogen must be taken into account.

In the general class considered, if the gas mixture and liquid were put in a closed container and left a sufficiently long time, the liquid would absorb the gas until the vapor pressure of the dissolved gas just equalled the partial pressure of the gas in the gas mixture. In case 1 this would be 100 per cent absorption, because the dissolved gas would exert a zero vapor pressure. Hence the partial pressure of the gas in the gas mixture would be zero, and the per cent gas would be 0 per cent. Since the volume of gas divided by the volume of gas mixture equals the partial pressure of the gas divided by the total pressure, then the per cent of gas in the gas mixture equals

$$\frac{\text{partial pressure of the gas}}{\text{absolute pressure of the gas mixture}}$$

In cases 2 and 3 the per cent absorption would

be something less than 100 per cent, depending on the nature of the gas and liquid. Suppose we express the nature of the gas and liquid by calling the theoretical percentage absorption, when the liquid and gas are in intimate contact for a sufficient time, at some imaginary standard condition,  $K$ . The theoretical absorption under some other condition may be called  $K'$ . Then  $K'$  may be increased (if it is not already 100 per cent) by increasing the total pressure on the gas mixture, since this increases the partial pressure of the gas, and hence the vapor pressure of the dissolved gas necessary to re-establish equilibrium. And the latter means increased concentration of the dissolved gas. Lowering the temperature of the system will in general increase  $K'$ , since lowering of the temperature gives a lowering of the vapor pressure of the dissolved gas. Increasing the concentration of the gas in the gas mixture will in general increase the amount of gas absorbed, since the partial pressure of the gas increases in proportion to the per cent composition. Lowering the concentration of the dissolved gas in the liquid will decrease the vapor pressure of the gas, and so increase the amount of gas that will dissolve. The value of  $K'$  can be found in the literature for most gases and liquids. Or, at least, information may be found from which a working value of  $K'$  may be obtained. Fig. 1 gives various values of  $K'$  at 60 deg. F. and 30 in. barometer, for certain concentrations of ammonia in the gas mixture and liquid. A family of such curves would be required to express  $K'$  for all conditions.

#### RATE OF ABSORPTION

This, however, does not tell us anything about the rate of absorption under any given conditions. In general, it may be said that the force which causes a gas to be absorbed by a liquid is the difference between the partial pressure of the gas in the gas mixture and the vapor pressure exerted by the gas dissolved in the liquid. With no difference the rate would be zero, and in order to get a rapid absorption of a gas in a liquid it must be understood that theoretically perfect absorption cannot be expected, that is, some difference in partial and vapor pressure must be allowed for.

The rate of absorption also depends on the intimacy of contact between the liquid and gas mixture, and this depends on the design and operation of the particular absorption power or spray system.

The per cent of the theoretical absorption realized depends on the rate of absorption and the duration of contact of the liquid and gas mixture, the latter also depends on the design and operation of the apparatus.

To sum up, the rate of absorption,  $R$ , for a given gas and liquid will be proportional to the product of the difference in partial and vapor pressures,  $D$ , times a factor expressing the intimacy of contact,  $I$ , or  $R = CDI$ . The per cent of theoretical absorption,  $A$ , will be proportional to the rate of absorption times the time of contact  $T$ , or  $A = C_1DIT$ , and the actual absorption for any gas and liquid will be proportional to  $K'$  times  $A$ , or actual absorption,  $P = C_2K'DIT$ .

This formula is not capable of any direct mathematical application, but may be useful in comparing various systems working on different gases and liquids, or for analyzing certain absorption problems.  $C_2$  is the proportionality constant, depending on the units in which the other factors are expressed, etc.  $K'$  is the theoretical absorption under the particular temperature, pressure and concentration of entering and exit gas mixture and liquid employed.  $K'$  will generally be fixed by plant operating conditions, and may be varied only by changing these.  $D$ , the difference in partial and vapor pressures, depends on these plant conditions; and also on the design of apparatus, in that for a given concentration of gas in the exit gas mixture and liquid, and for a given concentration of the entering gas mixture,  $D$  will have the effect of being larger with the counter-current flow principle than with parallel-current flow. The effective value of  $D$  with counter-current flow will depend on the number of spray systems or towers in series and on the number of effective zones in each unit.  $I$  and  $T$  will depend on the design and operation of the system as a whole. In-

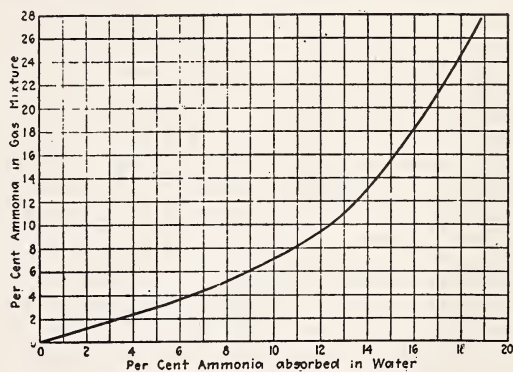


FIG. 1. CONCENTRATION OF AMMONIA IN GAS NECESSARY TO GIVE SOLUTION OF STRENGTH SHOWN. THEORETICALLY PERFECT ABSORPTION

creasing the liquid flow or circulation rates will in general increase  $I$ , the intimacy of contact, while increasing the volumes of gas mixture handled will decrease both  $I$  and  $T$ . This formula may be especially useful if a particu-



lar system is being used under known conditions and it is desired to know what it, or a duplicate system, will do under different conditions, say using a different gas and liquid. If the same conditions of flow rates of gas and liquid are to be maintained, the formula reduces to (1) per cent of absorption,  $P_a = C_s K'_a$ , and likewise (2)  $P_b = C_s K'_b$ , where the subscripts refer to operation under known or desired conditions. Substituting in (1) the known values will give a value for  $C_s$ .  $K'_b$  may be found from plant or published data. Then the product of  $C_s$  times  $K'_b$  will be the per cent absorption under the new conditions. Now suppose it is desired to use some other conditions of flow rates of gas and liquid. If the effect on the per cent absorption of varying these two factors is known for any fixed  $K'$ , when this is less than 100 per cent, then the  $K'_b$  we have obtained may be corrected to correspond. The results so obtained should be sufficiently accurate to act as a real guide in making new installations or to show plainly if some of the towers or systems in use are not giving the proper absorption, due to faulty construction or operation, or to offer a comparison of the capacity and efficiency of widely different systems.

The writer recently made some absorption tests using the spray system for liquid cooling.

Ammonia gas, from cylinders of liquid ammonia, mixed with air, was used as the gas mixture, and city water was used as the absorbing liquid. The per cent of ammonia in the exit liquid and in the entering and exit gas mixture was determined, and the temperatures of the entering and exit water and gas were taken, as well as data to compute the rate of flow of water. The rate of flow water and all temperatures were held practically constant, while the volume and percentage composition of gas mixture were varied. The composition of the exit gas mixture and water varied as a result of this. Fig. 2 shows the per cent ammonia in the exit gas mixture plotted against the per cent ammonia in the exit water from the spray system, as compared with the amount that would be found for theoretically perfect absorption. At first sight the relative value appears very large, but it should be remembered that the amounts involved are very small. The data shown here are important only in that they show that the per cent ammonia in the exit gas is largely determined by the per cent ammonia in the exit liquor. The curve for theoretical absorption is nothing more than values of  $K'$ , and since the absorption obtained is proportional to this, it follows that the absorption is taking place according to definite laws, and is not haphazard. If such a relation is found not to exist in any absorption tower or other system, it would be advisable to investigate the tower

filling or distribution of absorbing liquid for effective channels where gas is getting by without being acted on. Fig. 3 shows the total percentage of ammonia recovered by absorption plotted against the volume of gas mixture handled. In this spray system, and presumably in others, this was found to be one of the most important variables in operation. Increasing the volume of gas decreases the intimacy and time of contact, and so, other things being equal, naturally decreases the total absorption.

The increasing of the percentage of ammonia in the entering gas increased the percentage of total absorption in terms of the theoretical. The effect was small enough, however, to be nearly hidden by other variations in the test conditions.

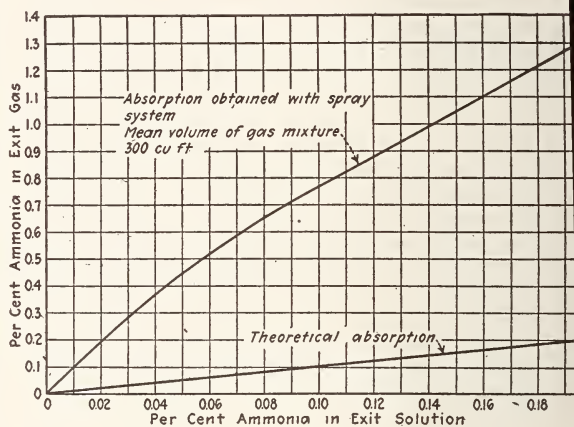


FIG. 2. PER CENT OF AMMONIA IN THE EXIT GAS AND SOLUTION FOR ABSORPTION OBTAINED WITH SPRAY, AND THEORETICALLY PERFECT ABSORPTION IN WATER

The flow of water used was such as to give nearly maximum absorption, and the rate of flow was not varied. The curves given are of general importance only in that they may be duplicated for existing installations, and comparisons drawn. In this case the curve in Fig. 3 shows practically the per cent absorption in general operation for this particular system, with flow rates of liquid of about 30 gal. per min. It is practically a series of values for  $C_s K' DIT$ , and since, according to the composition of the exit water reached, the theoretical absorption should be 99.8 per cent =  $K'$ , the curve practically gives values of  $C' DIT$ . In other words, if a given volume of any gas is to be absorbed in any liquid, from the curve in Fig. 3 can be obtained the absorption that may be expected for the volume of gas handled; i.e., for 300 cu.ft. per min., this machine would give 75 per cent of the theoretical absorption. This is the value of  $C_s DIT$ . Now, if the temperature and con-

centration of the exit liquid and entering gas are to be such that only 80 per cent of the gas may be theoretically absorbed, the value of  $K'$  will be 80 per cent. The actual absorption that will be realized will then be 75 per cent of 80 per cent = 60 per cent of the gas in the gas mixture. Suppose the gas mixture originally contained 50 per cent of the gas to

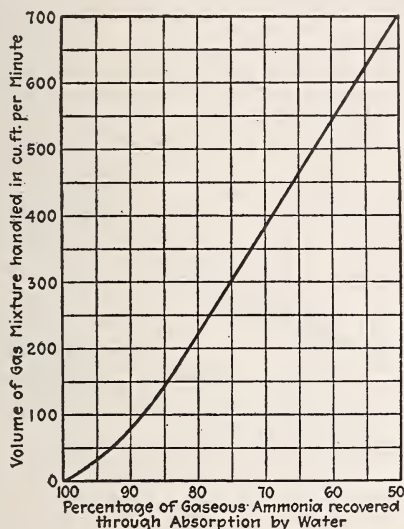


FIG. 3. RELATION BETWEEN VOLUME OF GAS MIXTURE HANDLED AND PERCENTAGE RECOVERY OF AMMONIA

be absorbed, or 150 cu.ft. Of this 60 per cent, or 90 cu.ft., will be absorbed and 60 cu.ft. will pass through. The exit gas mixture then has a volume of  $60 + 150 = 210$  cu.ft., and contains  $60 \div 210 = 28.6$  per cent gas.

Suppose this exit gas is passed through a second spray system, counter-current flow of liquid and gas mixture being used. Also, to simplify the problem, assume  $K'$  to remain unchanged, though in general it would increase in the successive spray systems. For 210 cu.ft. per min. the absorption would be 80.5 per cent of the theoretical, or the total absorption would be 80.5 per cent of 80 per cent = 64.4 per cent. The absorption in the second spray system is then 64.6 per cent of 60 cu.ft. = 38.6 cu.ft. The total absorption in two sprays is then  $38.6 + 90 = 128.6$  cu.ft. or  $128 \div 150 = 85.7$  per cent of the gas.

The exit gas from the second spray contains 150 cu.ft. of diluting gases and  $60 - 38.6 = 21.4$  cu.ft. of gas. This gives  $150 + 21.4 = 171.4$  cu.ft. of gas mixture, containing  $21.4 \div 171.4 = 12.4$  per cent of gas. Suppose this gas to be passed through a third spray system, counter-current principle. The absorption for 171.4 cu.ft. is 83 per cent of the theoretical, or the actual absorption is 83 per cent of 80 per cent = 66.4 per cent. The absorption in the third system is then 66.4 per cent of 21.4 cu.ft. = 14.2 cu.ft., making the total absorption in the three systems  $14.2 + 38.6 + 90 = 142.8$  cu.ft. and the recovery  $142.8 \div 150 = 95.2$  per cent. The results obtained are low, for a large volume of gas mixture was assumed, and in general the value of  $K'$  (which has been considered constant) will increase quite rapidly in the spray systems or towers having the more dilute exit liquid.

The last portion of this paper is subject to considerable elaboration, but this article has aimed rather at giving merely fundamental principles.

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University of Michigan.

## Tests on Small Engines at High Back Pressures

BY ALAN E. FLOWERS, R. J. PEPPER AND CROSBY FIELD

CALCULATIONS based on theoretical considerations covering a wide range of probable operating conditions such as it would be necessary to make in an attempt to get full rated output when employing high back pressures are given by one of the authors in *CHEMICAL & METALLURGICAL ENGINEERING*, Jan. 1, 1919, page 18, vol. 20. Results of tests on small steam-driven compressors operating under conditions different from those given herein, and yet which are frequently found in chemical plants, indicate that the curves may be applied as an approximate method of calculation to these conditions. The increase in

steam consumption with an increase in back pressure from atmospheric to 40-lb. gage in five widely different types of machines varied from 33 per cent to 58 per cent, with an average of 49 per cent. The governors operated on the throttling principle with cut-off constant, but all varied in design, and the quality of the steam varied, whereas the curves in former articles were based on either boiler steam pressure adjustment or variable cut-off and saturated steam. Nevertheless the figure for the increase in steam consumption on the curve most nearly applicable to these conditions was 50 per cent, which compares favor-



ably with the 49 per cent average value found. The actual results found are given in the curves herewith.

The units varied from 12.3 to 80.5 indicated hp. per 100 r.p.m. at full load, the average inlet steam pressure was 120-lb. gage, the average quality of the live steam was 99.2 per cent, while that of the exhaust steam was between 87 and 90 per cent.

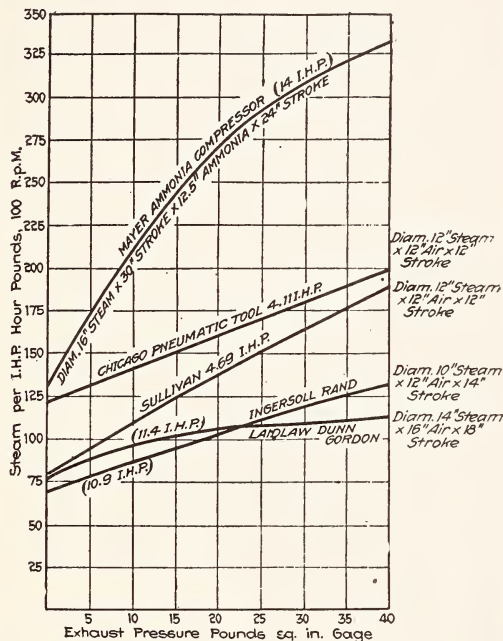


FIG. 1. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT NO LOAD

The equipment tested consisted of steam-driven air and ammonia compressors of several different makes and ratings. These units were operated exactly as they had been in normal plant operation except that the exhaust pressure was regulated and held constant at the three chosen values of 5, 20 and 40-lb. gage and the load held constant. Normal power plant units operate in actual service at 40-lb. gage back pressure, and these units have been successfully giving the service demanded of them during several years of operation. Air compressor units are equipped with fly ball type throttling governors, the output remaining fixed. One unit had its governor equipped to be controlled by the pressure of air in the compressed air system.

During the tests the air pressure was controlled by a valve manipulated by an observer stationed at a gage on the compressed air system.

During normal operation, the back pressure was governed by the demand for steam in the

40-lb. steam pressure system, additional steam being supplied when needed for the chemical processes either through an automatically operated reducing valve admitting live steam at 125-lb. pressure to the 40-lb. system or by manually operated valves. On the other hand, when the power demands were such that the exhaust steam of the power units was in excess of the immediate demands of the chemical processes, the plant operator discharged the excess into a hot well, where its heat energy was conserved in warming water. Any desired degree of closeness of control can be obtained by these means.

No heat reservoir was used in connection

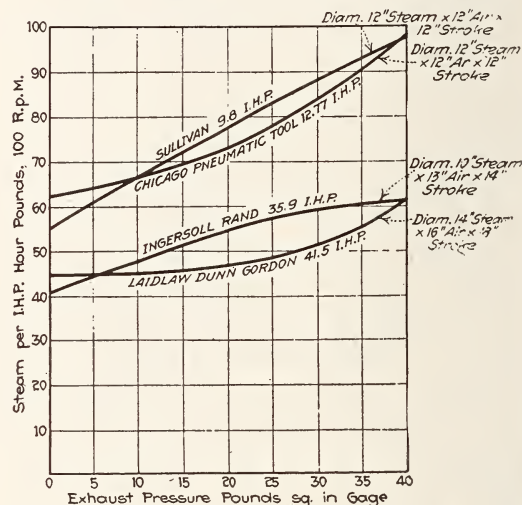


FIG. 2. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT HALF LOAD

with this 40-lb. steam system other than that afforded by the volume of the pipe mains. Reservoirs filled with hot water at the temperature of average steam pressure have been

#### TOTAL STEAM CONSUMPTION—FULL LOAD

Name of Compressor	I. hp. per 100 r.p.m.	Total Steam Consumption at Atmospheric Pressure and 100 r.p.m.	Total Steam Consumption at 40 Lb. Back Pressure and 100 r.p.m.
Ingersoll-Rand.....	51.9	2,025	2,690
Sullivan.....	12.3	685	1,087
Chicago Pneumatic.....	18.1	930	1,410
Laidlaw-Dunn-Gordon.....	59.7	2,150	3,140
Mayer.....	80.5	5,360	8,440

#### RATE OF STEAM CONSUMPTION

Name of Compressor	Steam per i. hp. at Atmospheric Pressure	Steam per i. hp. at 40-Lb. Back Pressure	Increase in Per Cent
Ingersoll-Rand (air)....	39	51.8	33
Sullivan (air).....	56	88.5	58
Chicago Pneumatic (air)	51.5	78	52
Laidlaw-Dunn-Gordon (air).....	36	52.5	46
Mayer (ammonia).....	66.5	105	58

used in connection with low-pressure exhaust steam-driven turbo units, and the use of some such reservoirs should be given serious consideration in any future installation. It should also be noted that moist steam, where the moisture is scattered throughout the distribution system, must act in a similar way in providing heat storage and consequent re-evaporation when needed even more effectively than a tank, because of the greater amount of evaporating surface available, provided the condensate be not completely removed from the system as fast as formed, but remains to some extent along the bottom of the steam mains or, still better, distributed in fine particles through the body of the steam.

The Mayer ammonia compressor was equipped and regularly operated with a fly ball governor acting through Corliss valve gear actuating an adjustable cutoff. This is the only unit tested equipped with a variable cut-off governor. During the test this unit was controlled in the same manner as the rest by throttling the steam. (One full load run on the Mayer ammonia compressor unit was made with the adjustable cut-off governor in action, resulting in a steam consumption about one-half that obtained with the throttle control.)

The general dimensions and data of the units tested are as follows:

Name of Unit	Steam Cylinder Diameter, Inches	Air Cylinder Diameter, Inches	Stroke, Inches	Piston Rod Diam., Inches	Steam Pipe Diam., Inches	I. hp. per 100 r.p.m.	Air Cyl. Displacement in Cu.ft. per 100 r.p.m.
Ingersoll-Rand.....	*10	13	14	1 1/2	3	51.9	215.5
Sullivan.....	12	12	12	1 1/2	3	12.3	155.6
Chicago Pneumatic.....	12	12	2	3	3	18.1	155.6
Laidlaw-Dunn-Gordon.....	14	16	18	2 1/2	4	59.7	468.0
Mayer.....	16	30	24	2 3/8	6	80.5	.....
(Ammonia).....	..	12.5	24	2 3/8	..	..	340.0

\*Duplex.

Operating speeds were usually from about 100 to 150 r.p.m. for the air compressors and about 35 r.p.m. for the Mayer ammonia compressor.

Steam was obtained from boilers that were supplying the entire plant, and the pressure varied somewhat during the tests, the amount of variation being determined by the usual works operating conditions. The average of the values for the steam pressure was used in working up the test results. It should be borne in mind that the load and exhaust steam pressures were closely observed and held constant, so that necessarily the same weight of steam was taken into the steam cylinder at each stroke regardless of the slightly variable boiler pressure. The only effect of a change

in boiler pressure would be a corresponding change of speed. The test results have, therefore, been reduced to a common constant speed

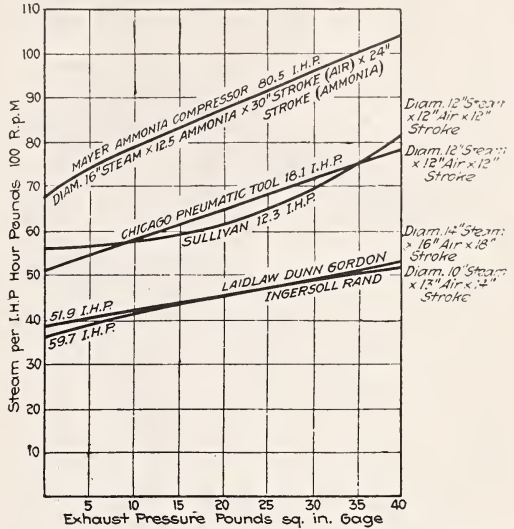


FIG. 3. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT FULL LOAD

and may be truly said to represent the steam consumption for the pressures recorded. This conclusion with regard to steam consumption

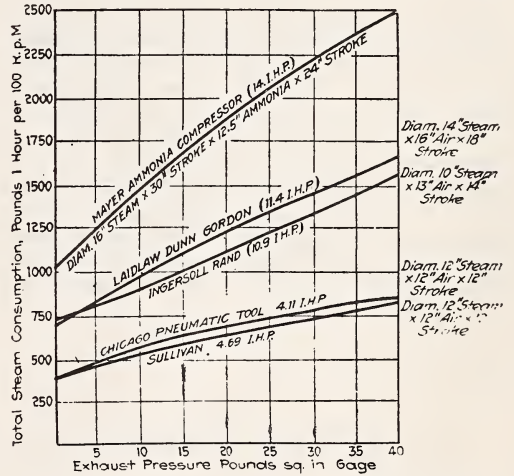


FIG. 4. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT NO LOAD

derived from theoretical considerations, as stated above, has also been checked and confirmed by plotting a number of the individual test values obtained at different boiler pressures and corresponding speeds. All the test results are based upon the carefully checked



weights of condensed steam. The scale accuracy was checked with standard weights before the tests were begun. The weight readings were checked throughout the course of each run by keeping the scale beam floating

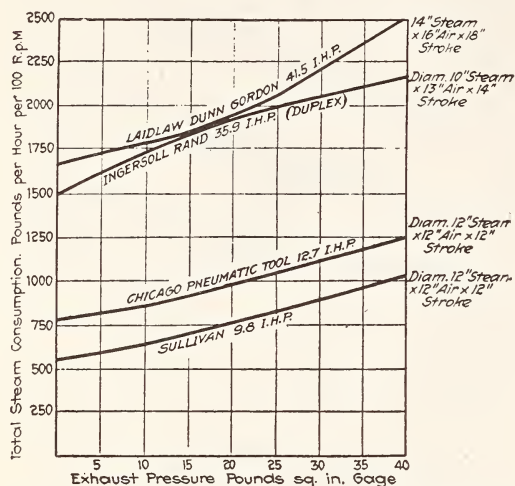


FIG. 5. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT HALF LOAD

constantly and recording the values at each 6-min. interval and comparing these with the total.

A totalizing revolution counter was used and readings were taken in three different ways. First, the speed was noted for 1 min. following each 6-min. interval, i.e., the difference between totalizing counter reading at beginning and end of each seventh minute. Second, the difference in totalizing counter readings at the beginning and end of each 6-min. interval was obtained. Lastly the total revolutions during the test were obtained as difference between readings at start and finish. The readings for 1-min. intervals were used only for check and

the values used in working up the test results were the average obtained from the total reading for each run.

Before the beginning of the test, the condenser was tested for tightness of joints, and

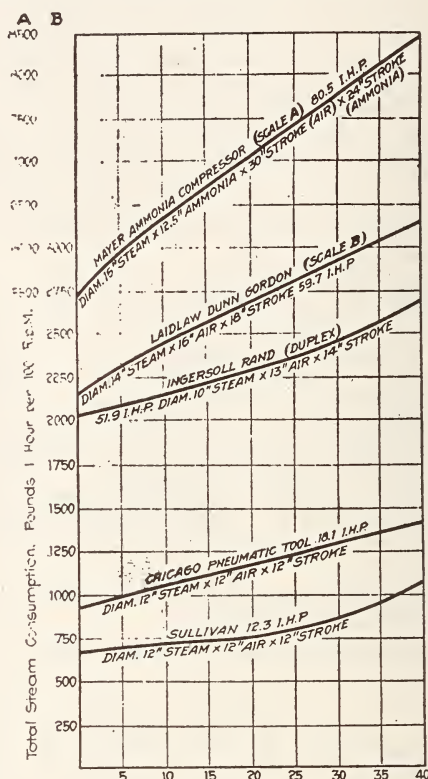


FIG. 6. EFFECT OF BACK PRESSURE ON TOTAL STEAM CONSUMPTION AT CONSTANT FULL LOAD

for leakage with 40-lb. pressure. Indicator cards were taken at each 6-min. interval and the indicated horsepower calculated from cards.

## Storage Tanks Made of Reinforced Concrete\*

BY F. W. FRERICHS

**A**BOUT a year ago it became necessary to construct large storage tanks for ammoniacal liquors. Usually such tanks are made of steel, but on account of the war steel plates were not obtainable and concrete was the next best material which was avail-

\*Read before the Chicago meeting of the American Institute of Chemical Engineers, Jan. 17, 1919.

able for the construction. By preliminary experiments it was proved that good concrete was not materially affected by crude ammoniacal liquor, and in order to ascertain the permeability of concrete walls by water and aqua ammonia four small experimental tanks were constructed and subjected to systematic tests.

The accompanying sketch (Fig. 1) illus-

trates the construction of the tanks, one of which was made from cement concrete consisting of one part cement, two parts sand, and four parts gravel. This tank was designated by the letter "A." The three other tanks were made from the same concrete mixture with the sole difference that in tank "B" 2 per cent hydrated lime was added to the cement before mixing, while tanks "C" and "D" contained 2 per cent each of two other waterproofing materials (stearates) of the market.

Each tank carried a gage glass on the side in which the level of the liquid in the tank could be observed. A sheet-iron circular cover was cemented to the top to prevent loss by evaporation. During the test period the tanks were standing in the open air exposed to the hot summer sun and the outside surfaces appeared dry. The inside area of each tank

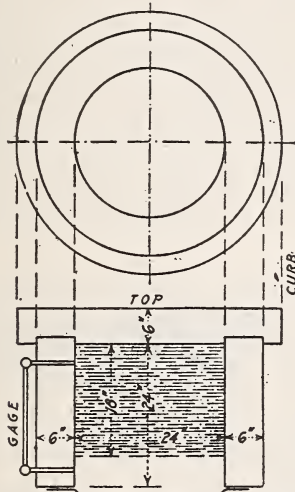


FIG. 1. SKETCH SHOWING CONSTRUCTION OF THE TANKS

was 15.70 sq.ft.; the outside area was 35.74 sq.ft.

After ten days' drying the tanks were subjected to the following tests with a view of ascertaining the permeability of concrete by water and ammoniacal liquor:

SERIES I.—PERMEABILITY FOR WATER

All four tanks were filled with water 18 in. high to within 6 in. from top, and the iron covers luted on tight with cement. Readings of water in gages were taken every day at 3 p.m. and the drop in the water level was recorded as read in inches.

Counting the decrease for the first day for saturation of the concrete, then the average evaporation per day per sq.ft. outside area of 25 sq.ft. has been for A 2.8 cu.in.; B 1.0 cu.in.; C 0.7 cu.in.; D 2.8 cu.in.

		I Temp.		II Drop in Surface			
		Max.	Min.	A	B	C	D
		Deg. F.	Deg. F.	In.	In.	In.	In.
1917	July 13	96	69	0.00	0.00	0.00	0.00
	14	81	67	0.63	0.38	0.13	0.75
	15	84	67	0.75	0.38	0.19	0.94
	16	83	68	1.00	0.38	0.19	1.19
	17	82	64	1.19	0.50	0.38	1.38
	18	83	68	1.38	0.50	0.38	1.50
	19	86	69	1.56	0.56	0.38	1.63
	20	90	68	1.69	0.63	0.38	1.75
	21	90	69	1.81	0.69	0.44	1.88
	22	93	73	1.94	0.78	0.47	2.0
	23	87	67	2.06	0.88	0.50	2.13

Column I. Temp. max. and min. from Weather Bureau.  
Column II. Drop of level in gage in 1/100 inches.

		III Evaporation				IV Evaporation			
		A	B	C	D	A	B	C	D
		Cu. In.	Cu. In.	Cu. In.	Cu. In.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.
1917	July 13	285	172	59	339	11.6	6.9	2.4	13.5
	14	339	172	76	425	13.5	6.9	3.0	17.0
	15	452	172	76	538	18.0	6.9	3.0	21.5
	16	538	226	172	624	21.5	9.0	6.9	25.0
	17	624	226	172	678	25.0	9.0	6.9	27.1
	18	705	253	172	737	28.0	10.1	6.9	29.5
	19	764	285	172	792	30.5	11.4	6.9	31.7
	20	818	311	199	850	32.7	12.4	8.0	34.0
	21	877	352	212	904	35.0	14.1	8.5	36.2
	22	931	397	226	963	37.2	15.9	9.0	38.5

Column III. Evaporation in cu.in.  
Column IV. Evaporation in cu.in. per sq.ft. outside area of 25 sq.ft. exposed to atmosphere.

SERIES II.—PERMEABILITY FOR 18-IN. AQUA AMMONIA

All four tanks were filled with aqua ammonia 18 in. high to within 6 in. from top, and the iron covers luted on tight with cement. Readings of level in gage were taken every day at 3 p.m. and the drop of level was recorded in 1/100 in.

		I Temp.		II Drop in Surface			
		Max.	Min.	A	B	C	D
		Deg. F.	Deg. F.	In.	In.	In.	In.
1917	Aug. 6	85	68	0.00	0.00	0.00	0.00
	8	85	71	0.31	0.31	0.13	0.25
	9	78	64	0.56	0.44	0.25	0.38
	10	76	60	0.94	0.50	0.31	0.44
	11	80	63	1.25	0.56	0.38	0.50
	12	79	65	1.38	0.63	0.44	0.56
	13	84	66	1.50	0.69	0.50	0.61
	14	83	68	1.75	0.71	0.56	0.63
	15	80	69	1.81	0.73	0.63	0.67
	16	86	71	1.94	0.75	0.69	0.71
	17	91	72	2.06	0.81	0.75	0.75

		III Evaporation				IV Evaporation			
		A	B	C	D	A	B	C	D
		Cu. In.	Cu. In.	Cu. In.	Cu. In.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.	Cu. In. per Sq.Ft. Outside Area.
1917	Aug. 6	140	140	59	113	5.6	5.6	2.4	4.5
	8	253	199	113	172	10.1	8.0	4.5	6.9
	9	425	226	140	199	17.0	9.0	5.6	8.0
	10	565	253	172	226	22.6	10.1	6.9	9.0
	11	624	285	199	253	25.0	11.4	8.0	10.1
	12	678	312	226	276	27.1	12.5	9.0	11.0
	13	791	321	253	285	31.6	12.8	10.1	11.4
	14	818	330	285	303	32.7	13.2	11.4	12.1
	15	877	339	312	321	35.1	13.6	12.5	12.8
	16	931	366	339	339	37.2	14.6	13.7	13.7

Columns I—IV designate the same as in series I.



The aqua ammonia in the tanks did not perceptibly decrease in strength in the ten days' test. The tanks were exposed to the hot sun.

Counting the decrease of the first two days for saturation of the concrete, then the average evaporation per day per sq.ft. outside area exposed to the atmosphere (25 sq.ft.) was for A 3.5 cu.in.; B 1.0 cu.in.; C 1.25 cu.in.; D 1.02 cu.in.

After these tests were made the tanks were dried out and painted on the inside with three coats of raw gas tar. The tar used for the first coat was thinned down with about 10 per cent turpentine, which caused the tar to penetrate about one-eighth of an inch into the concrete. After one week's drying the tanks were tested again with ammoniacal liquor and during several months there was no appreciable loss of their contents.

### THREE STORAGE TANKS

Encouraged by these results three large storage tanks were built by plans which were prepared by Messrs. Brenneke & Fay, civil engineers of St. Louis, who describe them as follows:

Three tanks were built in a concrete pit 47 ft. 2 in. wide, 130 ft. long and 30 ft. deep. The excavation for the pit was made in the

slope of the river bank partly in earth and partly in solid rock. The bottom, side and end walls rest on solid rock. The walls of the pit are designed as vertical reinforced concrete slabs, their bottom edge being heeled into a trench cut in the rock and the top edge reinforced with a flange acting as a horizontal girder. The tops of the walls are tied across to the opposite walls at intervals by a system of longitudinal and transverse beams which are reinforced to act in either tension or compression, these beams being supported at their intersections by columns from the bottom of the pit. The walls of the pit are so reinforced as to resist hydrostatic pressure in either direction. The north and east walls, which are the upstream and river walls, are also designed to resist the impact of running ice during a high water stage.

After the side walls were built the bottom of the pit was covered with concrete to make it tight, and is reinforced with steel in both directions as a precaution against any upward pressure that might occur during high water on account of fissures or cavities in the rock underneath. In the concrete bottom, sumps are provided to collect rainwater, seepage or leakage from the tanks. Circular chases were also left in the concrete bottom in which to

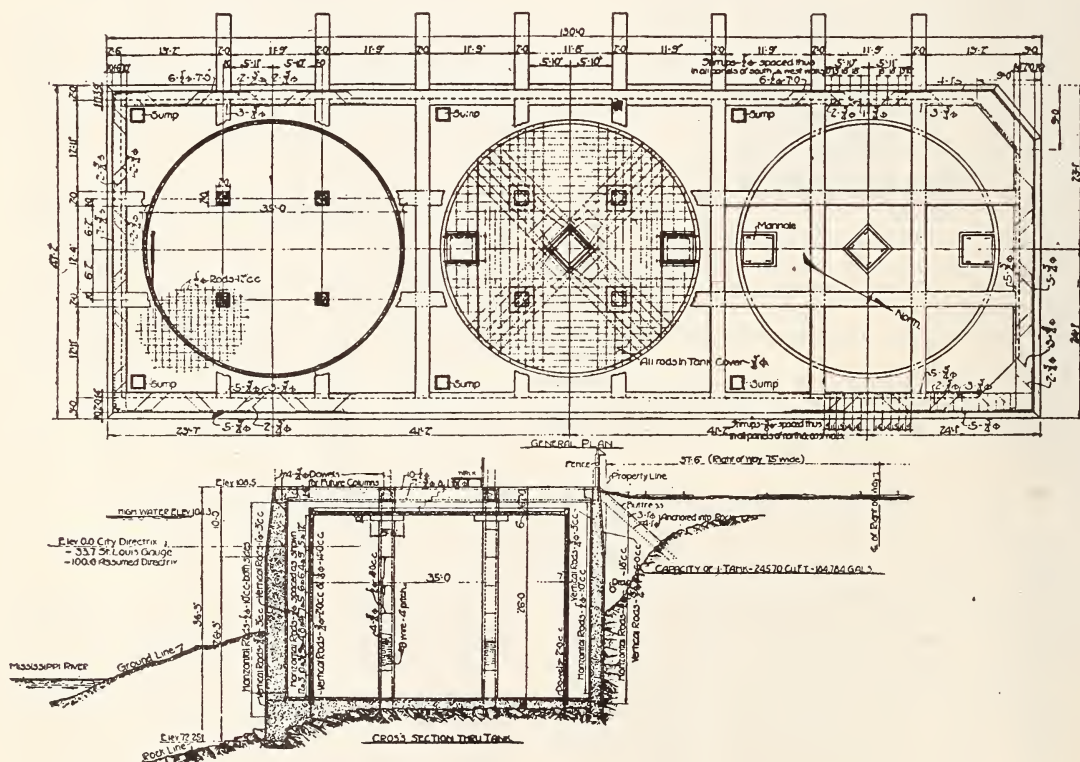


FIG. 2. PLAN SHOWING GENERAL DESIGN, DIMENSIONS AND DETAILS

heel the side walls of the tanks in order to get a tight joint between the walls of the tanks and the bottom. The longitudinal and cross beams between the walls at the top of the pit are also designed to support a concrete floor should a building be constructed over the pit in the future. All concrete work in the pit is composed of one part red ring portland cement, two parts sand, and four parts washed and screened Meramec gravel. The accompanying plans (Fig. 2) show the general design, dimensions and details, as well as the steel reinforcement of both the pit and tanks.

The three tanks are 35 ft. inside diameter, and 26 ft. deep. The walls are 7 in. thick, and the tops are covered with a concrete roof 6 in. thick. Manholes are provided in the roof of each tank and are constructed with a double curb of concrete 6 in. high around the openings. The manholes have metal covers in the form of an inverted pan, the edges of which rest in the groove between the curbs, and the groove is filled with water to form a seal to prevent the escape of gases from the tank.

The roofs of the tanks are also constructed with a curb about 6 in. high around the edge so that the entire roof can be covered with water as an additional seal against the escape of gases through the concrete.

#### PLAIN CONCRETE TANKS WATERTIGHT

As the tanks are to contain ammonia liquor it is essential that they should be tight. Preliminary to their construction several small experimental tanks about 3 ft. in diameter were built with and without waterproofing compounds mixed with the concrete. The plain concrete tanks apparently were as watertight

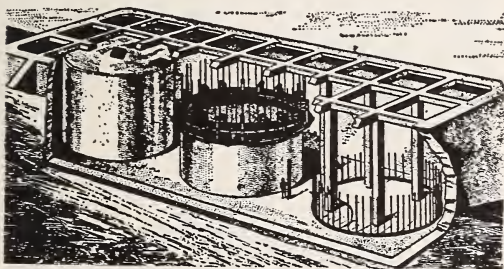


FIG. 3. PERSPECTIVE DRAWING OF THE THREE TANKS

as those in which compounds were used. From the information obtained from these experimental tanks, and from various other sources, it was concluded that waterproof tanks could be built of plain concrete. It is essential that all joints in the walls be eliminated and the concrete be mixed dry, that is, of a consistency of a stiff mortar and then thoroughly rammed. In order to eliminate all joints it was neces-

sary to arrange to concrete continuously day and night from the time the walls were started until they were finished. The vertical reinforcing rods were first secured in position, sixteen of which were 1½-in. diameter plain rods located equidistant around the circle, the balance of the rods being ¾-in. diameter deformed rods.

On each of the 1½-in. vertical plain rods was placed a metal sleeve constructed with a pair of metal jaws so arranged as to grip the rod wherever the sleeve was placed. The outside of the sleeve was threaded full length and provided with a large nut. From these sleeves were suspended wooden yokes having a metal bearing on the nuts on the sleeves. To the yokes were attached the sliding forms for the tank wall and also the working platform for the men.

The general construction of the yokes, forms and platform is indicated on the accompanying perspective drawing (Fig. 3). The forms were about 5 ft. high made in sections bolted together. The faces were made of quarter-sawn tongued and grooved material laid vertically. After the horizontal reinforcing for the lower 5 ft. of tank was wired in place, the forms were placed and concreting started. The concrete was delivered by a chute from the mixer at the top of the pit to the working platform and deposited into the forms in thin layers and thoroughly tamped. As soon as the concrete reached the top of the forms, the movement of the forms was started by turning up the nuts on the threaded sleeves. This work was carried on continuously day and night, no stopping in the work of concreting or movement of forms being allowed from the time of starting until the wall was finished.

The placing of the longitudinal reinforcing steel was carried on at the same time. As soon as a nut reached the top of its sleeve the load on it was relieved and the nut backed down to the bottom and the sleeve slid up the rod and secured to a new position, and the process of jacking continued. The movement of the forms was made uniform by taking an equal number of turns on each nut in rotation. The rate of movement varied from about 8 in. per hour during the cool hours before sunrise to about 14 in. per hour during the heat of the day, as the time of setting of the concrete was affected by the temperature of both materials and atmosphere. After the top of the wall was reached and the concrete set, the forms were disconnected and removed and used again on the next tank. The concrete roofs were put on at a later date after the walls were thoroughly set.

The concrete in the tank walls is composed of one part red ring portland cement, two parts sand and three parts washed and screened Meramec gravel.



After the concrete work was completed and the tanks dried out the bottom, sides and roof on the interior were coated with three coats of tar applied with a brush as an additional precaution against leakage of liquid gas.

The tanks were then tested by filling with water. In the walls of the first tank built there was some leakage through slight lifting

cracks which was due to the slow movement of the forms. These lifting cracks were avoided by more rapid movement of forms on the balance of the work. The leaks gradually healed up and have practically disappeared.

The capacity of each tank is about 185,000 gal., and cost approximately \$10,000 exclusive of the tank pit.

## Future of Industrial Organic Chemistry

BY HAROLD HIBBERT

WITH regard to the late war it may be accepted as a truism that the peace and safety of the whole world rested on a far-reaching knowledge of the underlying principles of scientific and technical chemistry.

A review of our chemical knowledge, both scientifically and applied, shows that prior to 1914 the chemistry of the aromatic compounds had been moderately well developed in this country, while that of the aliphatic had been more or less neglected. The reason for this is probably traceable to the influence of the German school of thought. Inasmuch as there existed in Germany large supplies of the raw materials necessary for the production of aromatic derivatives such as toluene, benzene and naphthalene, from which dyestuffs and pharmaceutical products are manufactured, it was natural, in view of the world markets obtainable for these finished materials, that this field should have been developed much more intensively than that of the aliphatic compounds such as the products from wood distillation, grain alcohol, fats, oils, gasoline, etc., all of which were imported products. Not only this, but the dyestuff industry forms, more than any other, the pivot around which so many different manufactures revolve.

In addition, it has always been tacitly assumed that the aliphatic compounds, especially those of saturated character such as the hydrocarbons (gasoline, etc.), are relatively inert materials, and consequently much less "plastic" than the aromatic derivatives; in other words, less capable of being transformed commercially into other products of industrial importance.

### FOUR MAIN DIVISIONS OF WAR REQUIREMENTS FOR CHEMISTS

If we review the war requirements, we find that they may be divided, in so far as the chemist is concerned, into four main divisions:

1. Foods and food products.
2. Medical and pharmaceutical supplies.

3. Explosives and their intermediate derivatives.

4. Poison gases.

A consideration of these shows that the aliphatic chemical compounds have played a rôle equal, if not superior, to the aromatic derivatives. In consequence, university professors, graduate students and technical chemists have, in many cases for the first time, been able to acquire a deep and far-reaching knowledge of the properties of aliphatic substances. If during the last forty years we have specialized on the technical application of the aromatic bodies, it is because it "paid to imitate Germany," but the prediction may now be made with safety that the industrial progress of the next half century will be intimately associated with the development of the chemistry of the aliphatic products.

A consideration of the subject will show that our necessities, comforts and luxuries are all closely related to products of the former class. This is clearly proved among other things from a consideration of the immense capital tied up in the manufacture of products of an aliphatic character. Thus with regard to foodstuffs, we have the vast industry of the edible oils, palm, coconut, cottonseed, soya bean, peanut, fish oil, etc.; and closely allied to this, the cyanamide fertilizer industry.

For our heat and light, we require gasoline and candles. Our clothing is derived from cellulose, either in the form of cotton or as artificial silk. Of our medical supplies, it is only necessary to mention such materials as glycerine, methyl and ethyl alcohols, formaldehyde, paraldehyde, chloral, etc. In the matter of luxuries, the moving-picture industry depends on a supply of cellulose derivatives either in the form of nitrate or acetate, while in the late war the most deadly of the various toxic gases employed was the so-called "mustard gas," which in addition to the products already mentioned is also a representative of the aliphatic series.

## VALUE OF ALIPHATIC MATERIALS

Some idea of the value of these materials may be obtained from the following figures:

Value of cotton crop (1918) <sup>1</sup>	\$1,616,207,000
Value of natural gas (1917) <sup>2</sup>	142,089,334
Value of products of wood distillation (1914) <sup>3</sup> .....	10,236,332
<hr/>	
Domestic production of vegetable oils (1917) lb. . .	2,159,335,000
Domestic production of animal and fish oils (1917) <sup>1</sup> lb.	1,636,451,000
Domestic production of butter (1917) lb. ....	1,369,500,000
<hr/>	
Total, lb. ....	5,165,286,000

The imports of fats and oils in 1917 amounted to 636,288,306 lb., while 584,254,000 lb. were exported. If we compare these with a total value of \$40,044,427<sup>2</sup> for the entire output of crude coal tar products (tar, light oils and naphthalene) for 1917 the difference is striking.

The edible oil and fat industry is one of the first magnitude, and yet it will be admitted that the scientific principles regarding the hydrogenation of vegetable oils were first developed scientifically in France, then technically in Russia, Germany and England, and last of all in this country. As in the case of many of the most important technical developments, the work may be traced in its original conception to the scientific researches of Frenchmen, in this case Messrs. Sabatier and Senderens.

While it may be allowed that this country has carefully followed the European patent situation, and endeavored to take advantage of it and improve on the same, yet in so far as the main general scientific aspects are concerned, it has shown relatively little scientific originality. Thus while celluloid is distinctly an American invention, the underlying scientific facts connected with the manufacture of stable nitrocellulose were largely developed through European studies. Without a knowledge of these fundamental properties it would not have been possible to proceed to the discovery that celluloid can be manufactured by compounding cellulose nitrate with camphor. The same holds true with regard to cellulose acetate and xanthogenate, the latter employed in the manufacture of artificial silk.

## UNIVERSITIES RESPONSIBLE FOR NEGLECT

There can scarcely be any doubt that the universities are in large measure responsible

<sup>1</sup>Figures supplied through kindness of Department of Commerce.

<sup>2</sup>Figures supplied through kindness of Department of the Interior.

<sup>3</sup>Figures supplied through kindness of Department of Agriculture.

<sup>4</sup>Figures taken from Bulletin No. 769, Department of Agriculture.

for the neglect of the study and technical application of the aliphatic derivatives. This neglect would seem to be to a large extent traceable to the faulty method of instruction, and the inability to make a student visualize the products with which he is called upon to deal. In other words, organic chemistry has been made a subject of "blackboard one-plane valency impressions" rather than a consideration of the energy and spatial relations of the constituent atoms in the molecule, and in this latter connection, it is difficult to understand why the work and theories of Michael have not been given much more prominence. The importance of training the student to visualize the spatial relations of the atoms in all organic compounds cannot be overemphasized. Instead of the customary procedure of showing the model of the carbon atom in the one or two isolated cases connected with stereoisomeric and optical derivatives, or in the case of the benzene ring, it would seem desirable to have available, at every lecture on organic chemistry, models which could be constructed so that the nature of the spatial arrangements would be at once apparent to the students, and instead of the customary one-plane representation, it would be possible for them to visualize at a glance the effect of the proximity of the atoms in the molecule and of the effect of the different forms of energy associated with the same, considered from the point of view of their spatial relations.

Thus all of the important properties such as substitution, ring formation, oxidation, reduction, etc., could be taught from this standpoint, and the value of an atom in the 1, 2, 3, 4, 5, etc., position relative to another atom attached to carbon, clearly defined and so thoroughly fixed in the mind of the student that, when called upon to advise on some process in connection with the manufacture of a synthetic product, he would never be at a loss to predict, at least in general terms, the nature of the material to be synthesized, and to indicate some procedure looking toward its successful manufacture.

While not wishing to detract from the interesting researches of Fry and Jones, or from the interesting discussions of Falk and Nelson, as well as of G. N. Lewis, it would seem, in so far as the technical side of organic chemical problems is concerned, that for the present the theories of Michael, though in some respects vague and indefinite, largely on account of the impossibility of providing all the quantitative data, yet at the same time do provide a working hypothesis which undoubtedly assists the research chemist to a remarkable extent in predicting the nature and course of chemical reactions and of the properties of unknown chemical individuals.

If a student learned to grasp thoroughly the

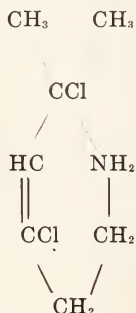


fundamental principles underlying the relative energy values of the atoms in the molecule, and to obtain a more profound and comprehensive knowledge of the facts of catalytic phenomena bearing on organic chemistry, he would be placed to-day in a far more advantageous position for solving the various technical problems arising in connection with the development of outlets for the commercial and industrial utilization of naturally occurring products found in this country.

#### PITFALLS OF THE YOUNG CHEMIST

The young research chemist in the industry is too apt to attempt to transfer his college knowledge of the "type properties" of any chemical compound to the derivative to be synthesized instead of realizing that the problem to be solved is in general one in which, for some reason or another, the "type property" has either ceased to exist, or has been considerably modified through the influence of certain groupings or atoms in the molecule. Thus he fails to realize that a reaction of any group such as carboxyl or hydroxyl, instead of representing a definite fixed property *per se*, is in fact rather a summation of properties representing a combination of the play of the various energies and affinities of the entire reacting atoms comprising the molecule; in other words, the group does not exist alone. It is this understanding and appreciation of the varied influence of each atom in the molecule on each other atom which enables the trained chemist to predict chemical phenomena and properties.

Much has been heard of the various psychological tests employed in the Army, and it would seem that equally satisfactory tests applicable to college men desiring research positions should be devisable. One suggestion in this connection is that at the conclusion of the usual course of organic chemistry a series of semina exercises should be given in which, by the use of models, the students should be called upon to give indications of their ability to predict the nature and properties of different chemical compounds. Thus, for example, with a compound of the formula



the student could be asked to set up the carbon models, and then, with these in full view, he asked to predict the effect of various reagents on the various atoms in the molecule; in this case, the tendency toward ring formation, the action of alkalis, effect of oxidizing agents, removal of halogens, properties of the different hydrogen atoms, etc. A satisfactory answer to such questions would, from the technical research standpoint, provide evidence much more valuable of the man's probable research ability than reams of paper dealing with his knowledge of the dozen different ways for making, let us say, ethane or other derivatives.

The fact that acetaldol can be made by the condensation of acetaldehyde with alkalis, etc., and the various conditions which must be observed in carrying out such a reaction are of less importance than the ability to predict, for example, just in what manner, say, acetaldehyde would condense when mixed with some other aldehyde, for instance, isobutyric aldehyde.

The same is also true of the ability to foresee, for example, the point at which substitution will occur when a hydrocarbon, for instance, propane, hexane, etc., is subjected to the action of bromine, etc., or again where it will occur in the case of acids and acid chlorides.

These problems and many others of vital interest and importance are to be found discussed at length in the published work of Arthur Michael.<sup>5</sup>

#### THE TRAINING OF THE PROFESSOR

So much for the training of the chemist. With regard to the training of the professor, it would seem that he also stands in need of overhauling. In the first place he has been, from time immemorial, both badly underpaid and overworked, and both of these conditions call for urgent and vigorous action. No professor or instructor can undertake research work unless he is

1. Competent to undertake the same
2. Has adequate facilities in the way of post-graduate men and equipment
3. Has the necessary time to devote to it
4. Is adequately recompensed so that he can be free to devote himself to the scientific side of the subject without the necessity of burdening himself with onerous and uncongenial outside employment.

Granting this, there still remains the fact that the average university and college professor has hitherto not been in touch with the

<sup>5</sup>See, among others: *Journ. pr. chem.* 60, p. 286-409 (1899); 68, p. 487-520 (1903). *Berichte* 34, 626; 4028 (1901); 39, 2138 (1906). *Journal Amer. Chem. Soc.* 32, 991 (1910); 40, 1674 (1918); 41, 393 (1919).

problems of the industrial world. He has, in fact, many cases rather scorned any association with such, and naturally the industry has resented this and returned the feeling with interest. If the war has shown one thing, it is this, that the future generation of research chemists and chemical engineers will expect from their professors something more than a general knowledge of the theory of the subject, and will at least expect that they shall be conversant with the better known technical applications. As for the detailed knowledge, presumably this will be left to the director of the department of industrial chemistry, between whom and the professor of pure chemistry there should naturally exist the closest kind of personal friendship and scientific co-operation.

#### UNIVERSITIES TO TEACH INDUSTRIAL CHEMISTRY

Various universities, including Harvard, have now made a start in this direction by establishing departments of industrial chemistry, and it is to be expected that other universities such as Yale, Princeton, etc., will follow her lead. Unless this is done we shall undoubtedly fall behind other countries, as witness the marked progress being made along these lines in England and the subsidizing of English university professors by manufacturers of explosives and other chemicals with a view to utilizing the services of their highly trained intellects in the solution of different technical problems.

Various corporations in this country have already allocated considerable sums of money for similar purposes and it is now for the universities to decide as to how far they can, and will, co-operate with them in this. Instead of a series of Mellon Institutes dotted over the country, the more logical development would seem to lie in the creation of strong departments of industrial chemistry at the leading universities.

That there need be no lack of subjects requiring investigation is especially evident when we consider the natural resources of this country, and how closely their development is identified with a thorough knowledge of the chemistry, in particular, of the aliphatic compounds.

In this connection it may be of interest to take up the subjects indicated previously, namely:

1. Food products
2. Clothing
3. Fuel for light and heat
4. Medical supplies
5. Luxuries and arts,

and to glance briefly at the progress and de-

velopments which have been made regarding these during the last few years, and at the same time to indicate the general trend of future industrial development.

#### SLOGAN SHOULD BE "TOLERATE NO WASTE"

In the first place, in view of the recent prodigal waste of the world's resources, it is now necessary to "think internationally" as well as nationally. After all, the world's resources are not unlimited, so the slogan of the chemist from now on should be, "We shall tolerate no waste." As an illustration of this, if it can be shown that our entire supply of ammonia can be obtained from the coke oven gases, then it would seem logical to enact the necessary legislation to enforce the introduction of the recovery system to the entire coke industry, while other processes, such as the manufacture of cyanamide, which encroach on our limited available supply of coal and power should, if necessary, be excluded from the manufacture of such material.

In the same way if we can produce the country's requirements of alcohol and acetic acid economically from such materials as waste wood, which it must be admitted seems rather unlikely, then from the "world conservation standpoint" these processes should logically receive more attention than when prepared by other methods involving the use of raw materials, limited in extent and capable of being adapted more effectively and efficiently to other branches of the arts. In this connection it is also true that the manufacture of ethyl alcohol from waste pulp sulphite liquors, if possible from a commercial standpoint, is also true conservation when considered from the point of view of the utilization of food-stuffs such as corn, etc., for the same purpose.

What can the technical chemist do to assist in bringing down the high cost of living? How can the universities, colleges and scientists assist him? A brief attempt will be made to answer these questions. Concerning the list previously quoted, namely, food products, clothing, light and heat, medical supplies and luxuries, an examination will show that they are arranged in approximately the order of their importance with regard to the development and protection of the individual.

#### FOOD PRODUCTS

For the first time in their lives millions of people have been forced to learn, during the last four years, something regarding the nature of food and food products. As is well known, the bodily requirements comprise three main divisions, namely, fats, carbohydrates and protein, a shortage of any one of which proves disastrous.

With regard to fats, these are aliphatic compounds, esters of glycerine and fatty acids,



and owing to their utilization along lines other than for food, a very pronounced world shortage soon occurred in this field after the outbreak of the war. As is well known, fats are utilized for the manufacture of glycerine and fatty acids, the latter being converted into soap and various other useful chemical products, while the glycerine finds its main outlet in the manufacture of explosives, cordite, dynamite, etc.

An increase in the available supply of edible oils thus became imperative, and the production of cocoanut, peanut, palm, soya bean and other vegetable oils, together with animal fats, was stimulated to a very marked extent, and yet in spite of this the shortage abroad remained very acute. All of these oils represent aliphatic derivatives, regarding which much research work is necessary and from which, in turn, marked technical advances may be expected. Thus soya bean oil is comparatively a new product and is produced now in such large quantities that additional outlets for the material are desired. In 1918 we imported from China and Japan 335,983,492 lb., having a value of \$35,454,639.

The properties, chemical, physical, etc., of peanut oil would seem to repay investigation, and the general question of prevention of rancidity in oils, especially in the case of cocoanut and palm oils, is a subject calling for the attention of the chemist. A good cheap commercial method has been developed for the deodorizing of fish oil so that the low grades, which on account of their high fatty acid content cannot be used for purposes of hydrogenation, can now be employed for the manufacture of glycerine and soap.<sup>6</sup> This question of the hydrogenation of fatty acids is a field offering considerable scope for the research chemist, as is also the problem of the catalytic reduction of unsaturated aldehydes and ketones whereby unsaturated alcohols may be obtained.

The oils extracted from peach kernels and other waste raw materials have also been shown to provide useful substitutes for olive oil as salad dressings, etc., so that a more extensive use for these materials may be predicted.

#### CARBOHYDRATES

There also developed during the war period a considerable shortage in the supply of sugar, due in part to the inability to transfer supplies from one part of the world to another, notably from Java and other points. In consequence of this, the saccharine industry was developed both here and abroad, and some idea of the value of it may be gained from the

<sup>6</sup>It is stated that in consequence of the inability of trawlers to operate in the North Sea and other portions adjacent to the British Isles, the fish have multiplied very rapidly, so that it is expected the fishing industry will be very active during the next few years.

fact that at one time in England this material sold for about \$80 per pound, and it became customary for individuals to carry around small saccharine pills for the purpose of sweetening their beverages. In view of the fact, however, that saccharine is not a foodstuff, it is not likely that the manufacture of this material will be pushed to a considerable extent after the war except in the case of a few industries such as the mineral water trade, and up to the present no other substitutes have been developed and in fact they do not seem desirable. There would seem, on the other hand, to be a good opening for the development of special carbohydrate material capable of being assimilated by people suffering from diabetes.

#### PROTEIN

It is probable that in the domain of the protein foodstuffs most progress is possible. The extensive researches carried out, for instance, at Yale might well be utilized for the purpose of testing out the relative value of a pronounced protein diet in comparison with one entirely vegetarian. It would be of considerable interest to divide, say, a given class into two such squads, and then to have a full report at the end of a nine-months' period as to the mental and physical condition and development of the individuals in each series.

It does seem surprising that in view of the well-known facts regarding the protein content of peas, beans, lentils, cheese, etc., there should still exist doubt in the minds of college men, chemists and others that such materials are not adequate to provide the full protein requirements. When men of such eminence in the inventive world as Dr. Leo Baekeland and others testify that their best work was done on a strictly vegetarian diet, it provides considerable solid ground for the assumption that such conduct would also be of advantage in other cases.

In this connection a few facts concerning the soya bean industry may be of interest.<sup>7</sup> The bean itself is grown principally in China and Japan, and the development of the oil industry has been most marked within the last twelve years. In fact, had it not been for this commodity the probabilities are that many of the soap factories would have had to suspend operations during the last two or three years. It is claimed that this country could use some 600,000 tons of soya bean oil annually, corresponding to 6,000,000 tons of soya beans. In 1918 the total imports from Manchuria

<sup>7</sup>The data are compiled from an interesting article, "The Romance of the Soya Bean," by L. S. Palen, published in the January (1919) number of *Asia*, the journal of the American Asiatic Association. The U. S. Department of Agriculture Bulletin No. 439, "The Soya Bean," by Piper and Morse; and No. 769, "The Production and Conservation of Fats and Oils in the United States," by Bailey, also contain much interesting and valuable information.

were approximately 1,000,000 tons of beans, equivalent to 100,000 tons of oil. There were imported into this country in 1917 approximately 132,000 tons of oil, while the domestic production amounted to 21,000 tons.

Soya bean oil resembles linseed oil to some extent, that is, it is a drying oil and has been used largely in the manufacture of paints, linoleums and similar products. On the other hand, it is a valuable constituent of salad oils and butter substitutes and in China forms the staple food oil of large classes of the people.

Due to the fact that with ordinary methods of cooking soya beans remain rather unpalatable, their use, as such, has not been practiced to a great extent, but the various sauces, curds, cheeses, etc., made from it have been shown to possess such marked dietetic value that there is likely to be a rapid increase in the future consumption of these products which would tend to lower the high cost of living. Analysis shows the presence of:

	Per Cent
Proteins .....	30 to 46
Oil .....	12 to 24
Carbohydrates .....	24 to 28

According to Osborne and Randall,<sup>8</sup> "The proteins of the soya bean, unlike those of other leguminous seeds thus far investigated, are adequate for promoting normal growth . . . So far as we are aware the soya bean is the only seed hitherto investigated, with the possible exception of flax and millet, which contains both the water-soluble and the fat-soluble unidentified dietary essentials or vitamins."

However, it is not possible to enter into a lengthy discussion of the subject except to point out that the valuable results obtained in dietetic studies at Yale and other universities should be made more readily available and that at least one or two lectures on this subject should be devoted to the same in any college course on organic chemistry.

#### CHEAP FERTILIZER A NECESSITY

With regard to the whole question of food supply, it is necessary that cheap fertilizer should be provided, and the vigorous and active research being carried out with regard to the recovery of potash from blast furnaces and the cement industry, together with the various new methods for the fixation of atmospheric nitrogen, would seem to warrant the hope that considerable success may be expected from the experimental and technical researches at present in progress.

At present the Haber process would seem to be the cheapest method of nitrogen fixation, but it is rational to assume that the maximum

efficiency with regard to the arc process has not been reached, and that valuable improvements and developments may be expected along these lines. Furthermore the difficulties incidental to operating the Haber process at lower pressures are, as yet, far from being solved.

With regard to various by-products of the food industry, some outlet, for example, should be found for cottonseed hulls and similar materials. Preliminary experiments carried out by the writer appear to indicate that when compounded with nitrocellulose cork substitutes may be made, possibly applicable to manufacture of cork stoppers, lifebelts, etc., and this is only one of many uses to which this material might be applied.

Of other points of interest connected with the food industry, there is the question of obtaining suitable oils for use in the manufacture of tin plate and the "quenching of steel." Instead of the edible palm oil other cheaper material such as cottonseed, pine oil, etc., are apparently capable of substitution.<sup>9</sup> Finally, with regard to the extraction of oil from the oil cake, it is recognized that the best solvent for this purpose is trichloroethylene. This is obtained from acetylene and chlorine and is not manufactured in this country at the present time, although its synthesis is not a difficult matter to carry out commercially and it is to be hoped that domestic manufacture of the material will be undertaken.

With regard to the second item listed above, namely, clothing, we find on investigation that in addition to the use of cotton as such, the manufacture of artificial silk has been developed to a remarkable extent in this country in recent times. Furthermore, it was very evident during the last two years that the country's entire supply of knowledge regarding the scientific character and fundamental properties of certain cellulose derivatives such as the xanthogenate, and particularly the acetate, was decidedly limited in extent. It is a startling fact that while the value of cotton and cotton products such as nitrocellulose, artificial silk, etc., produced in this country is far greater than that of the rest of the world combined, yet so far as a hasty search of the literature shows there has not been a single outstanding scientific paper published in this country on the constitution of cellulose.

We have allowed the European countries to develop the scientific data on these subjects, and then made a feeble, belated attempt to obtain control of the technical applications either by purchase or otherwise. It is regrettable

<sup>9</sup>See Department of Agriculture Bulletin No. 769, page 23, "The Production and Conservation of Fats and Oils in the United States" (1919). This is a very valuable monograph, containing, as it does, the latest available information on the subject of edible oils.

<sup>8</sup>*Journal of Biological Chemistry*, December, 1917.



that in the case of the one or two large companies which have carried out scientific work in this field they should have felt under no compulsion to communicate the broad scientific results to the general body of chemists, but prefer instead to surround the matter with a complete veil of secrecy. It is not in this way that the progress of any industry can be assured, and fortunately as a result of the war, this would now seem to be much better recognized.

#### FUEL FOR HEAT AND LIGHT

When we consider the bearing of aliphatic chemistry on the question of heat and light, we find this country is by far the largest producer of petroleum and gasoline products, and not only this, but it is also the largest producer of benzol, of which advantage is now being taken in connection with gasoline mixtures for use in motor cars. There would also seem to be a valuable field in the development of materials of low nitration for admixture with kerosene for use as a motor fuel. Furthermore, it is a pity that there should still be any waste of natural gas, and this material would seem to warrant the close attention of chemists and technologists from both the scientific and industrial standpoint. The action of halogens, condensing agents, contact reactions with unsaturated derivatives, etc., are all interesting fields.

The cracking of petroleum has been developed to a remarkable extent, but it would seem that there is still room for processes involving the use of other contact materials which would enable this operation to be carried out at both a lower temperature and pressure. Possibly additional research would show the advantage of metallic chlorides other than aluminium. The reactions of hydrocarbons with sulphur chlorides would also repay investigation, and the interesting experiments recently carried out with nitrosyl chloride<sup>10</sup> possess much interest both for the scientist and for the technical chemist.

Prior to the war, this country was almost entirely dependent on Germany for its pharmaceutical supplies. In tracing the reason for this, one fact is quite evident, namely, the close co-operation which existed there between the universities and various pharmacological institutes on the one hand, and the industry on the other. Such well-known remedies as antipyrine, veronal, etc., were developed in university and not in technical laboratories. We still find it necessary to consult German text books and monographs for much of our information, and it now appears that the compilation and publication of such treatises on highly specialized subjects were carried out in many cases at public expense.

<sup>10</sup>*Journal Amer. Chem. Soc.*, Vol. 41, p. 368 (1919).

Is it asking too much that this Government should co-operate both actively and financially in the founding and support of a national pharmacological institute such as proposed by Dr. Charles Herty, and at the same time show its willingness to undertake the financing of the publication of scientific memoirs not warranted commercially through the usual channels?

#### INVITING FIELD FOR ORGANIC RESEARCH CHEMIST

The scientific development of the relation of constitution to pharmacological action is one of the most inviting fields for the organic research chemist at this moment, and it is highly desirable that there should be a much closer co-operation between the biologist on the one hand, and the organic chemist on the other. It would be a grave mistake, for instance, not to take advantage of the wonderful spirit of co-operation in this field, developed as a result of their combined activities in the domain to toxic war gases. It is for instance, inconceivable that the salicylates should represent the only type of compound best adapted to the use to which they are put, and it would seem extremely probable that active research would develop the use of better and more suitable products.

If for instance just one-half of the scientific work expended on the preparation and investigation of toxic war gases during the last two years were devoted to investigations looking to a remedy for tuberculosis, it is reasonably safe to assume that some cure would be found. In this connection it is necessary to recall the wonderful advances that have been made in the domain of biological chemistry, and referred to by Francis H. Carr in a recent lecture on "The Synthetic Organic Chemical Industry."<sup>11</sup>

#### CURE FOR CONSUMPTION POSSIBLE

For example, thyroxin, the principle contained in the thyroid gland, which regulates the rate of body metabolism, is now stated to be an oxyindole derivative of iodocyclohexane, and is so active that 0.3 mg. raises the body metabolism 1 per cent. The fact that thyroxin contains iodine is of considerable interest, since, as shown by the writer<sup>12</sup> and others,<sup>13</sup> a small trace of this element is sufficient to bring about the condensation of hydroxy, amino and imino derivatives. From the recent publication of Van Os<sup>14</sup> it would appear that the iodine present in thyroid preparations does

<sup>11</sup>*Journal, Soc. Chem. Industry*, Vol. 37, p. 425 (1918).

<sup>12</sup>*Journal, Amer. Chem. Soc.*, Vol. 37, p. 1748 (1915).

<sup>13</sup>*D. R. P.* 241,853; 250,326.

<sup>14</sup>*Pharm. Weekblad*, Vol. 55, pp. 1426-31 (1918); *Amer. Chem. Soc. Abstracts*, Vol. 13, p. 362.

not exert a marked influence, but in view of its remarkable activity as a condensing agent these results should not be regarded as final and conclusive. This is all the more necessary in view of the fact that in the case of tubercular patients the iodine content of the thyroid gland apparently varies appreciably from the normal, so that if some such connection could be traced, it might possibly provide a welcome guiding light as to a possible synthesis of a derivative capable of application to the cure of this terrible scourge.

When we consider broadly the nature of the products on which we depend for our enjoyment, we are again brought face to face with the aliphatic derivatives. The amusement of a large portion of the population at the present time is derived from moving-picture houses, and as is well known the films are made from cellulose nitrate or acetate. Our paper drinking cups and food containers are coated either with paraffine or nitro-cellulose and the casing of the sausage we eat is also probably a modified cellulose derivative.

No matter to what domain of the fundamental requirements of human activity, physical or social, we turn, it is evident that we are brought face to face with the properties and industrial applications of the aliphatic chemical compounds. Not only is it the duty of the chemist to develop the scientific and commercial application of such, but also to foresee and protect the individual from the harmful effects of abnormal natural and artificial conditions. Thus at the present time we are faced with national prohibition, and as this will render idle an immense amount of equipment, it is to this extent destructive of industry.

#### PROBLEM OF THE CHEMIST

The problem of the chemist is, therefore, to provide other outlets for this valuable machinery, and since the production of spirituous liquors is essentially a fermentation process, the attention of the chemist should naturally be devoted to new developments along such lines. Thus the manufacture of lactic, butyric and citric acids could be still further developed together with special sugars such as maltose and food products derived from these, for example, lacto-maltose, etc. The manufacture of special sugars could also be undertaken and it is natural to assume that there will be a much increased demand for essential oils and flavoring extracts for the soft drink industry.

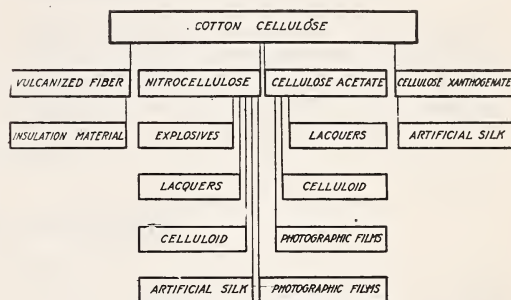
In the second place, one of the effects of prohibition will be to diminish the supply of fusel oil, in turn of amyl acetate, so that in all probability brewery equipment could be utilized for the manufacture of substitutes for these materials; in fact, certain cheap deriva-

tives of lactic acid would form useful substitutes for amyl acetate.

#### OTHER FIELDS FOR THE CHEMIST

It is not possible to more than mention other fields in which the services of the chemical expert in aliphatic chemistry can find a suitable outlet such as utilization of acetylene, sulphite pulp waste liquor, and especially in the utilization of waste wood products, etc., but the diagrams shown herewith are of interest as indicating the varied outlets for one raw material, namely, cellulose. These show outlets already developed, but indicate little or nothing of the vast unexplored territory still remaining.

Thus, with regard to nitrocellulose and cellulose esters generally, there is a very fertile field for a series of investigations relating to the question of solubility of these products in organic solvents through which much light might possibly be thrown on such problems as the physico-chemical nature of solution, the colloidal state, the theory of partial valency, etc. All of these await in turn the development of some theory as to the structure of the cellulose molecule. The chemistry of the cellulose esters is as yet a comparatively un-



known field, regarding which the industry is forced to rely almost entirely upon empirical data.

In another direction when we turn to the manufacture of celluloid in this country, the furtherance of the industry itself is dependent on the good will of the Japanese Government in selling us camphor. It would seem imperative on the part of the American scientific chemist and chemical manufacturer to solve this problem by undertaking the manufacture of synthetic camphor or by carrying out a vigorous search for substitutes for this material, or by doing both. In this connection it would be of considerable assistance and value to the research chemist if the celluloid companies would be willing to explain for their benefit something with regard to the special and peculiar properties which a true substitute must possess.



## THE WOOD DISTILLATION INDUSTRY'S FUTURE

In the utilization of the constituents of the oils obtained from wood distillation, there is an interesting field of vast extent open to the research chemist. In view of the difficulty which will be experienced in obtaining raw material in Europe during the next twenty or thirty years, it would seem that the wood distillation industry in this country is in an exceptionally favorable situation for development, and for the supply of products such as solvents for the varnish, artificial leather and lacquer industries; while as regards beechwood creosote, beechwood creosote carbonate, guaiacol, etc., the country should be self-sus-

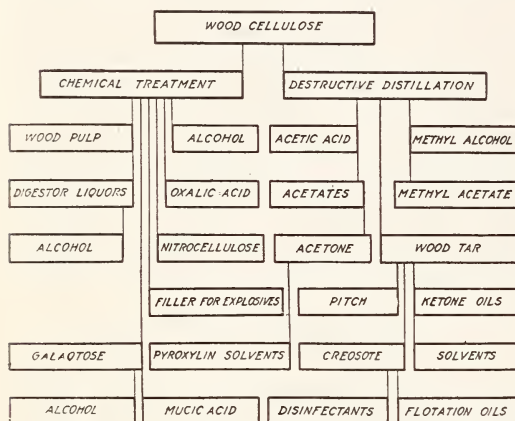
taining and not have to rely on foreign manufacture.

It is the function of the organic chemist to find outlets for the vast surplus production of aliphatic derivatives such as butyl alcohol, methyl alcohol, grain alcohol, acetone, etc., and to ascertain how far the new scientific facts developed during the last few years by the use of bodies such as phosgene, sulphur, chloride, aluminum chloride and of contact materials, for example, oxides of aluminium, thorium, nickel, etc., may be applied commercially.

In view of the extent to which the aliphate compounds enumerated above enter into all of our daily life, the importance of a thorough study of these cannot be overemphasized. To assist in this the university and college teachers must of necessity themselves have learned to grasp the fundamental facts concerning the nature of these natural products so that their students may be trained to acquire the habit of thinking of such not merely in the light of formulæ made up of so many letters and strokes, but as combinations of different forms of energy capable of the most diverse transformations.

The old idea of fatty hydrocarbons as inert material must also be relegated to oblivion, and the mind directed to ascertaining how far such products, by the employment of better known catalytic and other methods, can be rendered valuable to the industry.

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## Filtration and Filters\*

BY HENRY B. FABER

THE importance of filtration in industrial work has during the past three or four years been emphasized particularly in those chemical and industrial lines dealing directly and indirectly with products necessary for war. As we are approaching an era of expansion in all industries, and particularly so in the chemical industry, research and development will call for new methods of manufacture. A note of caution may properly be sounded at this time. Too often the technical man, carried up to too great an altitude by his chemical research, flies too high and neglects to give proper emphasis to the simpler operations, such as filtration, which act as the Scylla and Charybdis to wreck the chemical mariner.

From experience in the handling of a large number and variety of filtering problems, I

am inclined to classify them in two major groups.

First, those problems in which the slurries contain suspensions of a colloidal nature. These can hardly be dealt with except by highly specialized forms of apparatus and might even be regarded as a class not applicable to simple filtration. This group will, therefore, be passed over.

Second, those problems in which the solid suspensions may be separated from the liquid by the simple expedient of a filter medium. This latter group may be divided as follows:

Class A, which embraces those slurries in which the suspensions are fine, but not of a colloidal character. This group includes those slurries which contain slow filtering suspensions in large bulk or small bulk, and those slurries which by reason of a relatively small amount of suspended matter require merely clarification.

Class B embraces those slurries containing

\*Extract from address before the Fifth National Exposition of Chemical Industries, Chicago, Sept. 25, 1919.

relatively free filtering suspensions, which permit the liquid content to be separated readily from the solids, where the solid content is of considerable bulk, crystalline or definite in its form.

Class C embraces those slurries which are principally mother liquors, containing relatively large crystals, in which the liquid content can be drained readily, the crystals washed easily, the principal problem being the automatic and easy handling of the solids.

The filtration engineer has designed various types of filtering equipment to be applied to these various groups. A description of their types and their limitations as applied to the various groups will, I believe, be of interest, together with a short sketch of the development of these various types.

#### FILTERS FOR CLASS A PROBLEMS

In class A of group II, in which the suspensions are fine and the slurries slow in filtering, the engineer has two problems confronting him—the problem of large area of filter surface and that of keeping the filter surface clean.

##### THE FILTER PRESS

The filter press is probably the best known type of filter equipment in use. The press consists of a series of shallow frames separated one from another by plates and nested together, forming a series of shallow chambers. Against the plates, which are channeled or scored with shallow galleries, are placed filter cloths, which act as the filtering medium. The slurry to be filtered is pumped into the chambers, the liquid forcing its way through the medium and making its exit by means of the galleries or grooves, leaving the solids deposited upon the medium and gradually filling up the chambers.

##### OPEN TANK LEAF FILTER

It remained to one George Moore, a metallurgist, to invent a process of filtration in the mining field which has had world-wide acceptance and renown. This process employed the use of filter leaves, operating in an open tank. These leaves were frames of pipe, usually rectangular in shape, over which was sewn filter cloth completely incasing the frames and forming a hollow shallow chamber with ribs spaced equidistant across the face of the leaf for the purpose of preventing the two faces of the cloth from touching. The pipe constituting the lower edge of the frame was perforated. When the leaf was submerged in the slurry to be filtered and suction applied, this suction was translated throughout the entire space within the leaf, causing the liquid to pass rapidly through the cloth, leaving deposited upon the outside surface the

solids, in the form of an adhering cake. Many of these leaves were attached to a common header and in this form was called a "basket." The simplicity of this construction permitted the operator to throw into use very large areas of filtering surface at a relatively low cost.

##### SELF-DUMPING FILTER

At the time of this invention, George Moore anticipated that many problems would be encountered where a greater force than that exerted by a vacuum pull would be necessary to make the separations of solids from liquids. His original patents also called for the incasing of these filter leaves in some simple form of container for use by either suction or pressure. The self-dumping filters, so called, in which the container may be parted from the leaves, shortly made its appearance on the field, and met with wide acceptance in both the mining and industrial world. These filters, in which the basket of filter leaves is completely incased by a container permitting either suction or pressure to be applied to force the liquid through the medium, have a wide application in the many filtering problems of to-day.

##### COMPARISON OF THE VARIOUS TYPES OF FILTER

To sum up the virtues of these various types, the press, by reason of the fact that the filter cloths can be replaced readily, at a relatively low cost, protects the operator from serious curtailment in his filtering operations by reason of accidental damage to the cloths.

The open tank leaf filter has the advantage of large area of filtering surface and extremely low initial cost.

The self-dumping types of filters, by reason of the fact that they can use pressure as well as suction, have a wider latitude of use, but the same argument applies to them as applies to the open tank leaf type in that time is lost in re-covering the leaves, and repair and renewal are costly.

##### FILTERS FOR CLASS B PROBLEMS

In reference to the handling of problems in class B, viz.: those slurries which are relatively free filtering and build a substantial firm filter cake quickly, the rotary filter is the most desirable type to use.

The rotary filter made its first appearance in Belgium about 50 years ago or thereabouts, and consisted of a headed barrel rotating about its long axis. The face of the drum was perforated and a filtering medium was stretched around, completely encircling the drum, and held in place by winding cords. This machine was used for the filtration of salts and proved very effective. A gooseneck entered through the head of the drum, dipping down to within an inch of the bottom, and was



the means through which suction was applied to the interior of the drum. The drum rotated in a shallow container, dipping into the slurry through an arc of about 40 deg. Later this type of machine was built of sturdy metal construction. The perforated surface was replaced by bars of iron, forming a grating so that the drum had the appearance of a heroic-sized squirrel cage. In all cases, a gooseneck dipping within the drum downward to within a few inches of the bottom served as an exhaust and also to carry the liquid from the inside of the drum.

When rotating, the filter cake, which adhered to the surface of the drum, passed upward and over beyond the zenith, and was removed by means of a scraper.

It remained to the same George Moore who invented the Moore process of filtration to invent a multiple compartment or revolvable filter, which is the rotary filter of today. This filter, instead of being of the squirrel-cage type with a gooseneck outlet, has the peripheral surface of the drum composed of a number of shallow hollow compartments, over which is stretched the filtering medium. Each of these hollow compartments has its own separate pipe line connected to a valve hub by means of which suction or pressure may be applied at will, through any desired arc.

These machines have had wide usage in the mining field for the handling of concentrates and are extensively used in the industrial chemical field, where automatic and continuous filtration is rapidly replacing the batch or intermittent method.

### Filters for Class C Problems

In handling slurries of the character mentioned as class C, viz.: crystals from mother liquid or coarse granular suspensions, the centrifugal or draining boards have been widely used.

#### ROTARY HOPPER DEWATERER

The rotary filter has failed in many cases by reason of the fact that the solids will form too heavy a cake and will not adhere firmly enough to prevent the cake breaking away from the drum and thickening in the container. The rotary hopper dewaterer is a type of filter machine built especially for this class of work, and consists of a series of elongated hoppers arranged radially about a central axis, each hopper having a filter bed, below which a pipe line connects with the central valve hub, similar in design to that used in the construction of the rotary filter. As the filter beds are set quite a distance below the rim of the hoppers, they form in reality a series of filter trays, revolving slowly about a central axis. The slurry is fed into these trays at a point about 30 deg. from the zenith

and dewatered by means of suction as they rotate through an arc of about 40 deg. Suction is then automatically cut off and the product discharged either by gravity or by a puff of air, making the operation continuous and automatic.

### Practical Suggestions for the Engineer

#### SETTLING SHOULD PRECEDE FILTERING

In a great number of the ordinary filtering problems, settling should precede the operation of filtering, or the slurries should be thickened by some means until the amount of suspension has reached the maximum permissible for easy handling. Suspensions will settle at a relatively uniform rate of fall until they thicken to such an extent that they begin to clump. It is usual to consider the rate of settling as uniform until the particles approach one another by a distance less than five times their diameter, at which point the settling rate begins to slow down very rapidly. A simple test that is often made in the laboratory is to permit the slurry to settle freely and plot a curve, showing the widening of the clear supernatant liquor. A point will be noticed in the large majority of problems where the curve shows a marked slowing down of the rate. It is at this point that we find it desirable to complete the separation by filtration. Too often the engineer attempts either to settle completely his slurries or to filter completely his slurries, where a combination of settling and filtering will give a much more efficient operation. This is a general statement, but one which will bear emphasis.

#### EXPERIMENTAL FILTER FOR CLASSIFYING FILTRATION PROBLEMS

The class in which a particular filtration problem belongs may be determined easily by using a small experimental filter leaf constructed as follows:

Bend a small piece of  $\frac{1}{4}$ -in. brass pipe in the form of a square paddle with sides approximately  $3\frac{1}{4}$ -in., perforate the lower side and stitch over the frame either unbleached muslin, No. 10 duck or other suitable filtering medium. Strips of wood about the thickness of a lead pencil are inserted between the faces of the cloth in order to prevent collapsing. The filter leaf is now complete. By vacuum rubber pipe 2 or 3 ft. in length, the leaf may be attached to a graduated Woulff bottle, which in turn should be connected up to the suction line. Introduce into a battery jar or large beaker the slurry and submerge the filter leaf. When the suction is turned on, the liquid will pass through the leaf into the Woulff bottle, leaving deposited upon the face of the leaf the solids. Note the time, quantity and character of the liquid constituting the filtrate and the thickness and character of the

filter cake produced for the given period of time. The filter leaf with the adhering cake when withdrawn from the slurry may be introduced into a receiver containing wash water, and the wash water drawn through in the same manner as the filtrate. The amount of water necessary to wash the cake can be readily measured, the period of time necessary for washing obtained, and the dryness of the cake determined by allowing the filter leaf with adhering cake after being withdrawn from the wash water to be held suspended in the air until the occluded liquid has been sucked out of its pores. A filter leaf of the above-mentioned size will have approximately one-sixth of a square foot of active filtering surface, and when a ratio is struck between the volume of filtrate or weight of cake to one-sixth of a square foot for the particular period of time employed, the operator can readily calculate the number of square feet of active filtering surface he will need for an installation capable of handling a given quantity of liquid or solid. He will also be able to determine the amount of wash water, the purity of his cake and moisture content of the latter, which will closely approximate the results he will obtain on a commercial installation.

#### DEDUCTIONS FROM EXPERIMENTAL TESTS

From these tests a few general deductions can be made. If it takes a longer time than ten minutes to form a filter cake of at least  $\frac{1}{4}$  in. in thickness, in all probabilities the problem falls into class A, in which are included the filter press, open tank leaf filter and the self-dumping filters. If a firm cake of from  $\frac{1}{4}$  in. to upwards of 2 or 3 in. in thickness can be formed in less than ten minutes, and if the cake frees itself readily from the leaf, a rotary filter will very likely handle the problem. In determining the size of the rotary filter by this simple test required for any problem, it must be borne in mind that any point on the peripheral surface on the filter drum will require from one to ten minutes to pass through the full 360 deg. according as the machine makes one r.p.m. or one-tenth r.p.m. Consequently, as frequently less than one-half of the surface of the drum is submerged continuously in the slurry through which it rotates, the requirements for filter surface for continuous operation must be multiplied by approximately two, as less than one-half of the drum is active for cake building. If in making the tests a cake builds so rapidly on the filter leaf and the product is of such a granular nature that in attempting to withdraw the leaf from the slurry the cake will not adhere, but slough off, the centrifugal or the rotary hopper dewaterer will most likely be the type of machine for use.

#### SUGGESTIONS ON WASHING

Often it is as important to wash the solids as it is to filter them, and a few suggestions along this line may be in order. Irrespective of the type of filter used, the one important factor to provide against is the channeling of the filter cake. In the filter press as well as the self-dumping type it is difficult to provide against a classification of the solids, as the heavier particles will often settle away from the lighter, forming areas of less resistance to the passage of the filtrate. This classification is not met with to any noticeable extent in the open tank leaf type of filter, as the slurries may be kept in constant and thorough agitation during the process of filtration, thus insuring a homogeneous slurry. Consequently, it has been my experience that washing on the open tank leaf type of filter can be accomplished with less wash water and a more thoroughly cleansed product obtained than by either the press or self-dumping type. It seems to be a prevailing custom among engineers to determine the degree of wash that a filter cake has been subjected to by merely testing the wash water coming from the filter. Let me suggest to those who are operating different types of filters, to sample the filter cake itself. Without a doubt, in many instances surprisingly curious results will be obtained. In sampling I do not mean the ordinary grab sample, but a number of samples taken from different parts in the chamber or on the filter leaf. In many cases it will be found that the most astonishing results are due to channeling.

Another important point on the subject of washing is that we do not get the advantages of diffusion to the extent desired by passing our wash water through the cake, and it has been my practice to recommend wherever it is possible where extreme degrees of washing are required with a minimum amount of wash water to discharge the cake after the mother liquor has been replaced to a reasonable extent by wash water, and to churn up or cream the product, thus getting the advantages of diffusion and refilter. I wish to emphasize this method of washing, particularly in the case of the rotary filter, where the period of washing is relatively short, and where much is left to be desired where filtering and washing and automatic discharge are accomplished in one revolution of the filter drum. Most gratifying and surprising results have been obtained on difficult problems of washing where only a sufficient amount of wash water is sprayed upon the cake to replace the mother liquor held by the cake volume for volume, and the cake discharged into some form of agitating tank in which it is creamed up with wash water in sufficient amount to permit of easy handling of the slurry and refiltered.



One other important point before closing the subject of washing is, in dealing with free alkalis, the passage of steam through the cake prior to washing with water will often show very beneficial results.

#### IMPORTANCE OF AMPLE PUMP CAPACITY

Why it is that the engineer after recommending the purchase of expensive installation will suddenly take it into his head to economize on the size of the pump, and particularly the size of the pump lines in connection with vacuum filtration, has always been a mystery to me, and yet it is a fact. Allow me to emphasize the need of ample pump capacity. In the filtration of bicarbonate of soda the pump displacement should be from 10 to 15 cu.ft. per minute of free air per sq.ft. of active filtering surface unsubmerged. This amount of free air per sq.ft. decreases rapidly as the porosity of the cake decreases. Carbonate of lime or caustic lime mud from the ordinary soda-lime process requires only from 3 to 5 cu.ft. per unit square area of filtering surface. Another point that the engineer seems to neglect to take into consideration is that short suction lines are preferable to long lines. In one instance I have in mind a 500-ft. suction line, which, al-

though of adequate diameter, failed completely to function, due to its extreme length.

#### CONCLUSION

In concluding, allow me to offer a few suggestions to the manufacturers and chemists who have filtering problems to solve.

Filtration is too important a factor in the operation of any plant, where the separation of solids from liquids is a step in the operations, to neglect careful, faithful research on the most practical means of obtaining the separation. These problems cannot be brushed hastily aside or decided hurriedly, but should entail the same thoroughness in research that any technical chemical operation deserves. One of the most important points to emphasize is that in many cases filtration will not be as difficult an operation if more care and attention are given to the form in which the solids appear at the time that filtration is to be attempted. In other words, the chemical reactions should have run their course and the suspensions should have been allowed to form themselves in a physical condition as far as practical, giving the best separation possible in consideration of their nature and crystalline structure.

## Brine Corrosion of Petroleum Equipment

BY RALPH R. MATTHEWS AND PHILIP A. CROSBY

PETROLEUM coming from the Healdton Field, Oklahoma, contains salt water in varying proportions, and also a small amount of sediment or silt. Most of the silt is very finely divided and when separated from the oil has a powder-like appearance. The salt water separates from the petroleum very slowly, and on standing in a tank for six months or even longer from 0.2 to 0.4 per cent is still present.

Just why the water is held in the oil so tenaciously is not exactly clear, but it appears that the finely-divided silt is in suspension in the oil and helps to support and retain the water. Due to this close association of the salt water with the petroleum, some of it travels through the pipe lines to the refineries, even though it may be in storage in the field for a considerable time. Thus the oil will probably arrive at the refinery containing 0.5 to 1.5 per cent of B. S. & W<sup>1</sup>, as determined by dilution, and whirling in an electric centrifuge

<sup>1</sup>B. S. & W. is an oil man's term and is interpreted as bottom settlings and water. Thus it really means the per cent of water, silt and other foreign matter in the oil.

at approximately 1,200 r.p.m. Our experience has shown this B. S. & W. is 60 to 75 per cent salt water.

To the uninitiated it no doubt seems easy to remove the salt water by washing with good, clean, warm water, or by adding a chemical which will precipitate the objectionable salts from the water and in turn from the oil. The difficulty arises here in getting an intimate mixture between the water or aqueous solution and the tiny drops of water in the oil, which probably have a protecting oil film around them. Chemicals which break down this surface tension and would thus free the drops of water have been successfully applied to the treatment of B. S. from tank bottoms, but their application to crude oil has not given the desired results. It is probable that the large volume of oil in comparison with the small amount of water is responsible for the negative results obtained. Various methods of electrical dehydration have also been applied to recovering oil from B. S. and petroleum of high water content. The reduction, however, is generally not below 1 per cent B. S.

& W., thus leaving too large amount of the objectionable salt water. The centrifuge will probably reduce the B. S. & W. to 0.3 to 0.4 per cent, but its application is expensive, and there would still be enough salt water remaining to cause the trouble indicated below.

A typical analysis of the brine shows the following figures:

	G. per liter: Grains per U.S. Gal.	
SiO <sub>2</sub> .....	0.008	0.44
R <sub>2</sub> O <sub>3</sub> .....	0.127	7.42
CaCO <sub>3</sub> .....	0.074	4.33
CaSO <sub>4</sub> .....	0.011	0.64
CaCl <sub>2</sub> .....	4.275	249.72
MgCl <sub>2</sub> .....	1.526	89.15
NaCl.....	61.140	3572.20
Total solids.....	67.161	3923.90

The above indicates approximately a 6.5 per cent solution of sodium chloride, and special attention is directed to the content of magnesium chloride.

#### OBSERVATIONS OF CORROSION

The results outlined here were obtained at a refinery where the petroleum is pumped through stills and heated to the desired temperature. The mixture of oil and vapors passes into an apparatus which allows the vapor to separate from the residual oil (fuel oil.) The vapor then passes through a series of dephlegmators, where it is fractionally condensed. Thus from the top of the last dephlegmator the lightest vapor passes through a condenser and the gasoline flows from there into the receiving house. Lines lead from the other dephlegmators through coolers and into the receiving house, where the necessary "cuts" are made.

The dephlegmators are arranged with water coils in the top, and after a few months' service these coils began to leak. Later the tubes of the condensers started leaking water into the gasoline. Investigation showed excessive corrosion had taken place and one hole over an inch in diameter was found in a water coil when the dephlegmator top was removed.

Some of the rusty deposit found at the points of worst corrosion was removed to the laboratory and examined. It gave a slightly acid reaction and consisted largely of ferrous iron and chlorides.

#### ACIDITY OF OIL VAPORS

On the bottoms of the last two dephlegmators were steam lines and valves which had never been used. The lines were at the lowest points of the bottoms and any aqueous condensate would have a tendency to collect in them. There was a slight leak around the valves on these lines and a deposit showed a distinctly acid reaction and was found to consist mostly of ferrous iron and chlorides. Thus

the indications pointed to corrosion by hydrochloric acid, and in order to try further to substantiate this theory a water line was tapped into the top of the next to the last dephlegmator. By means of it a small amount of water was forced down through the up-coming oil vapors. The water was trapped out in the receiving house and a sample obtained. This was examined in comparison with a sample of water taken before going through the dephlegmator and was found to have acquired an acidity equal to 8.23 grains of HCl per gal. of water.

Laboratory distillations of the oil were made, using a glass flask, and the water recovered was found to contain a small amount of hydrochloric acid. In one extreme case enough acid vapors came over during a laboratory distillation to turn blue litmus red when it was moistened and held at the mouth of the bottle containing the gasoline. The water recovered in this case was titrated, and calculation showed that the acid formation would be at the rate of 0.012 g. of HCl per liter of oil.

In view of the above evidence there seemed little doubt hydrochloric acid was responsible for the rapid corrosion, and the next step was to locate its source.

#### ACTION OF MAGNESIUM CHLORIDE AT HIGH TEMPERATURES

In looking for the source of the hydrochloric acid, the magnesium chloride in the salt water seemed most likely the cause. Molinari<sup>2</sup> states that "magnesium chloride volatilizes at a red heat and partially decomposes in the presence of minimal quantities of water, forming hydrochloric acid and magnesium oxychloride." This reaction starts at as low a temperature as 175 deg. C. If the reaction is carried to completion the ultimate products would be hydrochloric acid and magnesium oxide.

Stillman<sup>3</sup> says of magnesium chloride: "The latter compound, while not scale forming, is considered an active corrosive agent upon the supposition that at the temperature of 100 deg. C. and higher it is decomposed and hydrochloric acid formed and liberated."

The oil in passing through the stills is heated to approximately 260 deg. C., and at this temperature a large amount of the magnesium chloride present in the salt water in the oil is without doubt decomposed and hydrochloric acid formed. Then the acid vapors are carried with the oil vapors into the dephlegmators.

#### FINAL OBSERVATIONS AND CONCLUSION

It was noted that most of the corrosion took place in the last two dephlegmators and in the

<sup>2</sup>General and Industrial Inorganic Chemistry, p 527.

<sup>3</sup>Engineering Chemistry, p. 580.



condensers used with the last dephlegmator. It seems that is due to higher temperatures in the preceding dephlegmators. Thus in the next to the last dephlegmator the temperature drops to approximately 110 deg. C. and the most severe corrosion was noted on the water coils where there must have been a cooling below 100 deg. C. Some water vapor is always associated with the oil vapors, and it no doubt condenses on these water coils. The water readily collects the acid vapors and reaction starts on the metal at that point. Some of the acid vapors also carry over into the condensers, eventually causing them to give way.

We have noted this action from salt water in Healdton petroleum, but are of the opinion that petroleums from other fields could cause the same trouble, provided they carried even

small amounts of salt water containing magnesium chloride.

By way of summing up, the following may be stated as covering this case in brief:

Hydrochloric acid is formed from magnesium chloride in salt water present in Healdton petroleum during distillation.

Oil vapors which contain the above acid vapor cause corrosion and produce rapid deterioration of the fractionating apparatus.

With Healdton petroleum containing 1 per cent of salt water, the amount of acid produced may be as large as 3.39 lb. of hydrochloric acid per 1,000 bbl. of oil.

Acknowledgment is made to Dr. F. W. L. Tyderman, superintendent of this refinery, for encouragement and advice in carrying out this investigation.

Roxana Petroleum Co. of Okla.,  
Wood River, Ill.

## Air Conditioning in the Industries

By E. E. LEASON

AIR conditioning is becoming recognized as a subject of increasing importance by those who are interested in atmospheric conditions in factories, mills, laboratories, bakeries, tanneries, and the like, because the proper conditioning of air not only aids manufacturing processes but gives employees the proper air to breathe.

The possibilities of overcoming unhealthful air conditions are multitudinous. Among the most pronounced examples are chemical laboratories, bakeries, confectionery factories, film manufacturers' laboratories, lithography and printing plants, textile mills of all classes, and hide and leather establishments. The possibilities, however, of conditioning air are by no means confined to the industries just enumerated. Wherever there is "sick" air there is a remedy.

### SPECIFIC EXAMPLES

To be more explicit about the application of air conditioning systems, a few specific examples may be considered. For instance, in dye houses where no air conditioning system is installed the amount of fog or steam may be so great that a light will not show through it more than 30 in. away. The drip from the roof in such a room is a nuisance and the drops of water collecting on the roof soon cause decay and deterioration. Furthermore, in a number of chemical industries the materials used are highly hygroscopic. This is true in the manufacture of gelatine products and explosives where it is imperative that

constant comparatively low temperatures and constant low moisture content be maintained. In other processes, those which involve oxidation, it is necessary that constant atmospheric conditions be maintained in order that the oxidation may be regular and rapid. This occurs more particularly in processes which involve the use of varnishes and paints.

Air conditioning is also a prime factor in the regulation of conditions in laboratories or manufacturing plants where very delicate tests are made. Balances which weigh to the fifth or sixth decimal place are affected by variations in atmospheric conditions. It is evident, by eliminating these variations, that tests, no matter how far apart, can be accurately compared.

### IN CANDY FACTORIES

In candy and chocolate factories, cool, dry air is an absolute requirement. If hard candy is kept in moist air for even a short period before being wrapped or hermetically sealed, the product loses its transparent color and resolves again into the appearance of granulated sugar; also the moisture makes the candy sticky and any particles broken off in the process of manufacture become affected in the same way. Automatic machinery is gummed up and eventually the whole factory must be closed down due to the fact that the machines cannot be run. If, however, moisture is taken out of the air and it is kept at a comparatively low temperature, the candy remains indefinitely as it was originally made and the

particles are as so much dust which may be collected by a vacuum cleaner, as it will be a dry sand-like powder. Chocolate candy which is made in warm moist rooms assumes the familiar gray color due to the working of the cocoa oils. In this industry, too, uniform low temperatures and low moisture content are prime necessities.

#### IN THE BAKING INDUSTRY

It is found that in the baking industry, a high humidity at a proper temperature maintained throughout the year will insure the baker standardized time for the rising of the dough. This is most essential where all baking and handling is done by machinery and thousands of customers wait each day for their fresh bread. The relief of a baker whose dough is ready for baking every day at the same hour can readily be imagined. The profit that results from having the bread ready at a specified time each day as compared to losses resulting from irregularity in deliveries makes an air-conditioning installation a paying investment.

#### IN PHOTOGRAPHY

Manufacturers and users of photographic films are being greatly helped by the proper conditioning of air. Films are made by a gelatine process and are therefore not only hygroscopic, but are soft and melt in warm humid air and must be dried at a low temperature and low humidity. Without manufactured air conditions the film manufacturer must depend upon favorable natural weather to produce films. Frequent forced shutdowns result because the weather is too hot or too damp. With artificially controlled atmospheric conditions, manufacturers of moving picture films, photographic paper and dry plates can operate 365 days in the year.

#### LITHOGRAPHING AND COLOR PRINTING

Successful lithographing and color printing where more than one color is used is dependent on air conditions. One of the most important points in work of this kind is the registering of the various colors so that they blend with one another. Every one has seen

pictures where this registering was not perfect. This results almost entirely from the expansion and contraction of the paper due to variations in moisture content in the printing room.

#### IN OTHER LINES OF INDUSTRY

In the textile, paper, chemical and drug, and meat industries, the maintenance of constant moisture content is a great factor of profit or loss. In these industries the manufacturers must protect their materials against loss of weight by loss of moisture. If textile fabrics, for instance, are allowed to become dry and are sold in the dry state, the manufacturer will lose a startling amount of money in a year. With cotton and wool at present prices one cannot buy the raw material with 12 per cent moisture in the case of wool and sell finished cloth with 4 or 5 per cent without taking a loss that would more than pay for an air-conditioning installation.

Furthermore, in the textile industry, silk, cotton and wool, static electricity is a source of constant worry to the factory superintendent, especially in winter. As the fibers pass over the machines, friction develops which causes the fibers to repel each other so that a close-spun thread or yarn with the fibers lying parallel does not result, producing, thereby, a product of inferior strength and resulting at the same time in the formation of a great deal of "fluff" or "fly." This "fly" floats around the room and is breathed by the operators. The way to overcome this condition is to add enough moisture to the air to make it a favorable conductor of electricity so that as soon as a static charge is formed in the product, it is drawn off and dissipated. Further, if enough moisture is present, the particles of "fluff" absorb moisture, become heavy and settle to the floor, where they may be readily swept up.

Equipment for air-conditioning is manufactured by the B. F. Sturtevant Co., Boston, Mass. Supplementing the manufacture of this apparatus the engineering organization of W. L. Fleisher, Inc., of New York City investigates industrial atmospheric problems.



## Calcium Molybdate as an Addition Agent in Steel Making

BY ALAN KISSOCK

**I**N THE production of alloy steel, molybdenum, like most similar metals, is commonly added to a steel bath in the form of a ferro-alloy, usually less than a half an hour before the furnace is tapped.

In the open-hearth furnace practice varies, from melting the ferro in a small electric furnace and making a hot metal addition, to crushing to about one-quarter mesh and adding it cold, or, as is perhaps most common at present, the alloy is thrown into the furnace, container and all, just as it comes from the manufacturer. In the electric furnace, with its more concentrated heat, the manner of introduction is of lesser importance.

Formerly a ferro containing from 75 to 80 per cent molybdenum was generally specified. Because of the difficulty of securing an ore suitable for manufacturing such a high-grade alloy, and because of the high melting point of the metal, with attendant difficulties of production, the cost of this alloy was necessarily high. In the continued attempt to decrease production cost, and since there can be no real objection on the part of the steel manufacturers, more recent practice has been to produce a ferro containing approximately 50 per cent molybdenum. This grade of ferro, besides being less costly to produce, is perhaps the principal factor in the success of its direct addition to steel. Its lower melting point is responsible for less segregation and eliminates the necessity of pre-melting or fine crushing.

In the attempt to create or stimulate the use of anything new, the first requirement is to establish its merit and secondly to decrease its cost. The first requisite—the value of molybdenum as an alloy for certain steels—is continually becoming better known. Principally from lack of demand, the war-time price of ferromolybdenum has fallen considerably, but if the metal is to find extensive use it is necessary that a reasonable and more constant cost be established.

In deposits of commercial extent, molybdenum seldom occurs in percentages sufficient to permit, even by the most efficient known means of ore concentration, a recovery of greater than 10 lb. of metal per ton of crude ore mined. Often considerably less may be extracted. A great many costs, therefore, must be charged against these few pounds of metal recovered, from the mining, through the often-difficult concentration, to the final transportation.

To these must be added the cost of electric

smelting with its heavy losses, even in the best of practice, the difficulties of coming within the customarily rigid specifications of the consumer, and the uncertainty of selling the product when finished. It is easily seen, therefore, that if a fair and reasonable return is to be made to the producer, ferromolybdenum cannot become cheap enough to compete largely with some of the more common steel-alloying elements. Assume that every possible cost of mining and treatment has been brought to its lowest point. Then if any further decrease in cost is to be obtained, it becomes possible only through some improvement in the metallurgical treatment or through the elimination of some step in the preparation of a suitable product for the steel manufacturer.

With these facts in mind, it occurred that it might be possible successfully to introduce molybdenum into steel by the use of a salt of the metal rather than by the use of ferromolybdenum. Could this be efficiently accomplished, then the electric-furnace reduction of ores and products would be eliminated and in its place a much lower-cost chemical treatment could be substituted.\*

### CHEMICAL COMPOUNDS AS ADDITION AGENTS

The idea of introducing an alloying metal into steel by means of some salt or compound thereof is not particularly new. It has been tried, both in the furnace and in the ladle, with certain of the metals, and with more or less success. Several difficulties, however, are encountered in considering the more common salts or compounds of molybdenum.

The ordinary 60 per cent molybdenite concentrate, or even the higher grade, is unfit for direct addition for several reasons. All such concentrates contain a certain proportion of silica and in basic furnace practice it is desirable to avoid, as far as possible, any introduction of silica into the bath. Upon addition of molybdenite to steel at least a portion of the ore would be converted into the trioxide and as such would readily volatilize and be lost. The most serious objection, however, is the 25 to 30 per cent sulphur content of high-grade concentrates. In a test made at the plant of the Southern California Iron & Steel Co. in Los Angeles, an attempt was made, by the addition of high-grade

\*Compare, for instance, J. P. Bonardi, "Notes on the Metallurgy of Wulfenite," *CHEM. & MET. ENG.*, vol. 21, p. 364, Sept. 15, 1919.

molybdenite, to introduce 0.4 per cent molybdenum into steel. It was found that although a considerable proportion of the molybdenum entered the steel, sulphur, with its great affinity for iron, was also introduced to the extent of 0.25 per cent. By long treatment in the furnace, with manganese and lime additions, this sulphur content might have been lowered, but with the furnace-man's constant effort to keep the sulphur low in his product, a molybdenite would hardly be looked upon with favor.

Roasted molybdenite concentrate or trioxide of molybdenum would serve as a direct addition agent, were it not for the ease with which this compound is volatilized. At 1,200 deg. F. the vapor pressure of molybdic oxide is quite high, so that recoveries from an addition at steel-furnace temperatures would be unprofitably low. Such roasted concentrates would also carry the silica gangue of the unroasted material, and though it is possible to manufacture a more pure trioxide, the cost of such is prohibitive.

Since molybdenum unites in varying proportions with oxygen, it is possible that one or more oxides might be found which would not be volatile at furnace temperatures. The difficulty, however, of efficiently producing such oxides makes such compounds of doubtful value for consideration as addition agents.

Sodium molybdate might serve as another possible agent but for the higher cost of producing it of a sufficiently high molybdenum content.

In the case of some molybdenum ores, a step between concentration and the manufacture of ferro involves either a furnace or a chemical treatment for the removal of possible impurities and the production of an alkaline salt of molybdenum, preferably calcium molybdate. Although in the production of ferro from molybdenite it is not always necessary to precede electric furnacing by a roast or wet treatment, such a process can be readily applied and a calcium molybdate of high grade very easily produced.

Theoretically, calcium molybdate should serve as an excellent addition agent to steel. It can be easily and comparatively inexpensively made of a high grade, containing practically nothing but the oxides of molybdenum and calcium. The salt is easily reduced and the lime apparently prevents loss by volatilization of the molybdenum trioxide. Upon reduction of the molybdenum, by the carbon or silicon in the steel, the lime would simply serve as a small added source of material for the ordinary basic slag.

Early in 1918, in New York City, several small steel heats were made. An experimental electric furnace was employed and molybdenum was successfully introduced by the use of calcium molybdate with a recovery of 95 per cent.

Encouraged by these tests and with the kind co-operation of P. E. McKinney, metallurgist at the U. S. Naval Gun factory, a commercial test was made at the Navy Yard in Washington, in September, 1918. The calcium molybdate was made from the wulfenite ores of the Mammoth Development Co. of Los Angeles, and furnished gratis by that company for the test. Using a Heroult furnace, six tons of scrap was melted and at the proper time sufficient calcium molybdate added to introduce about 1 per cent molybdenum into the steel. The molybdenum content of the product, as shown by final analysis, confirmed commercially the previous experimental results. At a later date, C. E. Margerum, metallurgist of the U. S. Naval Ordnance plant at Charleston, W. Va., repeated the success secured at the Navy Yard in Washington. A third electric-furnace test was made at the plant of the Carbon Steel Co. in Pittsburgh, Pa. A 6-ton Heroult furnace was employed, and a repetition of the success of the two previous heats gave ample assurance that calcium molybdate was a satisfactory addition agent for use in the electric furnace.

#### MOLYBDATE IN THE OPEN HEARTH

Having succeeded in these attempts, it was conceded that because of the strong reducing action of the electric furnace, the results obtained were to be expected. That the same success could be secured in the strongly oxidizing atmosphere and action of the open-hearth furnace was, however, open to argument, and considerable skepticism had to be overcome.

Experimentation has shown molybdenum to have less affinity for oxygen than either iron or carbon. Industrially, this is again proved by the fact that once in the steel bath neither "oreing down" nor "boiling" appears to lower the molybdenum content.

Provided the molybdate could come in direct contact with the molten metal, it was thought that the salt might be reduced either by the metallic iron itself or by one of its reducing constituents. By the courteous aid of the officials of the Carbon Steel Co., 50 tons of pig iron and scrap was charged into one of the basic open hearths at their plant in Pittsburgh during November, 1918. At the proper time sufficient calcium molybdate was added to introduce the desired percentage of metal. Analysis of the ingots produced showed a high recovery of the molybdenum added, and the success so obtained amply rewarded the effort expended.

Early in May, 1919, with the kind interest and co-operation of the staff of the United Alloy Steel Corporation, a second open-hearth test was arranged. Two 100-ton heats and a third but smaller basic furnace heat were made and the desired amount of calcium



molybdate added in each case. The practically complete recoveries of molybdenum secured proved beyond question that molybdenum in this form may be successfully, and very efficiently, introduced into steel made in the open-hearth. In all tests, rolling mill recoveries correspond with those usually obtained with the customary ferro addition.

In order that the molybdate may come in direct contact with the molten iron, it is necessary that the addition be made in the early stages of the heat. In one of the tests the molybdenum was in the open-hearth furnace over a 14-hr. period and under very severe oxidizing conditions. The fact that the molybdenum content remained practically constant is proof of another very important consideration in connection with the metal. It is conclusive evidence that molybdenum, like nickel, and unlike vanadium, "stays" with steel. In the use of molybdenum, therefore, the "crops" and scrap ordinarily encountered in all alloy steel manufacture can be remelted with but little loss, thereby reducing the amount of alloying metal required. Because of the economy that may be effected, the importance of this fact must be appreciated when considering molybdenum as an alloying metal to replace certain of the metals now being used, and for purposes in which it may serve equally well.

#### METHOD OF OPERATION

The introduction of molybdenum into steel by means of calcium molybdate involves no complications whatever, it being only necessary to bear the following in mind:

With the strongly reducing action and concentrated heat of the electric furnace, the time of addition is of less importance. Best results have been secured by introducing the molybdate immediately after skimming of the first, or phosphorus slag, the final or white slag indicating, of course, that reduction has been complete.

In open-hearth practice, the molybdate must be added in the early stages of the heat, not with the charge because of possible loss in the furnace bottom, but preferably a little before the melt becomes "level." In other words, in any type of furnace it is only necessary to remember that the molybdate must come in *direct contact with the molten iron*, and therefore in the basic open-hearth it must be added just before the lime begins to come up. A layer of slag would completely prevent contact with the metal. Shipped in sheet iron drums of convenient size, the molybdate is added, containers and all.\*

#### ADVANTAGES

From the standpoint of the miner the production of calcium molybdate is particularly advantageous. In almost every occurrence,

molybdenite is associated with considerable percentages of both iron and copper sulphides. In order to produce a marketable concentrate, all of the copper and a considerable portion of the iron must be removed. This may be accomplished by selective flotation, but this cleaning process not only adds to the operating costs but invariably means a lower extraction. In other words, any refining operation, whether it be in concentration or in the electric furnace production of ferro, is necessarily a costly one. Neither copper nor iron interferes in the production of calcium molybdate, so that the need of either of these refining operations is entirely eliminated. It therefore becomes unnecessary for the miner to make a high-grade concentrate or to separate therefrom any of the copper or iron sulphides that might be contained. The millman will readily appreciate the saving that may thus be effected.

The production of calcium molybdate offers a further advantage in that the equipment for its manufacture does not involve great cost nor is especial skill required in the operation. The method is comparable to the cyanide process in that large tonnages may be readily treated and in many cases such may be carried out right at the mine. The electric-furnace production of ferro not only requires very large expenditures for tonnage treatment, but also necessitates particular experience and skill. Only in rare cases is the mining company in position to carry out such an operation, and it thus becomes dependent on some metallurgical concern to put its product into marketable form.

Calcium molybdate is readily made, and with high recovery, from all molybdenum ores by simple chemical treatment. The salt as usually furnished carries approximately 40 per cent metallic molybdenum and contains no impurities detrimental to good steel manufacture. It has been proved beyond question that molybdenum, in this form, is a very efficient addition agent for the introduction of the metal into steel.

The particular advantage of the process is that a carbon-free molybdenum addition agent may be afforded to the steel manufacturer at a price which will assuredly permit the competition of the metal with those at present in more general use. It is not within the

\*All rights to the process as outlined, both in the United States and foreign countries, are covered in U. S. Pat. 1,300,279, and are owned by the Steel Alloys Co., Investment Building, Los Angeles, Cal. It has been arranged that license to use the process will be furnished gratis by the Steel Alloys Co. to any steel company that may purchase calcium molybdate from such molybdenum producers or sellers as may be specified upon the license. Since it is expected, however, that the arrangement mentioned will be made with all principal molybdenum producers, no hardship to the steel manufacturer, either in payment of royalty or limiting of purchasing power, will be effected.

scope of this article to attempt to point out the use or benefits of molybdenum in steel. The value of alloy steel in general is constantly becoming better appreciated. In the writer's opinion, molybdenum is the only metal commercially available in this country which is capable of developing in steels properties equivalent to those produced by metals which

must now be imported. A possible strategic value exists in the ample and constant domestic supply of molybdenum that is now assured. From the results of the work that is being done by concerns, as well as individuals of prominence, it is certain that molybdenum will shortly fill an important place in the alloy steel industry.

Los Angeles, Cal.

## A New Type of Catalyzer for Hydrogenation\*

BY W. D. RICHARDSON

THIS paper contains a description of mechanically prepared catalyzer for the hydrogenation of oils and for other processes in which metallic catalyzers are used, invented by Benjamin W. Elder, developed by W. B. Allbright of the Allbright-Nell Co., Chicago, and put on a practical operating basis in the writer's laboratory.

This catalyzer differs fundamentally in its method of preparation from catalyzers previously used and is not only of importance in a practical way but is of perhaps even greater scientific importance as a contribution to the theory of catalyzer activity. The process and product are covered by the Elder patents, assigned to the Allbright-Nell Co. of Chicago, Nos. 1,331,903, 1,331,904, 1,331,905 and 1,331,906 of Feb. 24, 1920, and by pending applications.

In March, 1917, there appeared at the laboratory of Swift & Co. a short, stocky, bronze-complexioned man of middle age who was introduced by W. B. Allbright, his companion, as Benjamin W. Elder, recently of Torreon, Mexico. This meeting was the result of previously made arrangements according to which Mr. Elder's process was to be further developed and worked on a practical commercial scale.

Mr. Elder brought with him the simple and primitive appliance which was one of those by which he first proved that an effective and active nickel catalyzer for the hydrogenation of oil could be made by the action of an abrasive upon bulk nickel.

### INITIAL WORK ON GRINDING NICKEL

This apparatus consisted of a nickel plate about 12 in. square and  $\frac{1}{8}$  in. thick, firmly fixed by screws placed at the corners to a wood block of the same dimensions and  $\frac{3}{4}$  in. thick. The other member of his apparatus consisted

of a metal sheet or plate measuring about  $2 \times 2\frac{1}{2} \times \frac{1}{8}$  in. and screwed to a wooden handle. In order to operate with this apparatus Mr. Elder coated the plate with an oil, such as cottonseed oil, placed thereon a sufficient amount of abrasive, such for example as 200-mesh ground sand or silica, and then, by a process of rubbing the small plate upon the large one with the oil and abrasive between, produced in time finely divided, mechanically prepared, metallic nickel, which upon trial proved to be an active and effective catalyzer for the hydrogenation of oils.

This was not actually the very first apparatus used by Mr. Elder. An earlier one is described in a letter to the writer dated at Los Angeles, April 6, which reads in part as follows:

It was the unpleasant and dangerous experiences that I had encountered in reducing catalyzers that first made me think of trying to produce "nickel in a finely divided state" mechanically.

Observing closely the oil from a journal bearing encouraged me to give more thought to the subject. I noted that the abraded metal in the waste oil was so fine that it was difficult to thoroughly remove it from my hands.

I finally concluded that what I would really have to do was to design some method of grinding the nickel in the oil that I intended to harden while the oil was hot in a tank that was supplied with hydrogen. I was living in Torreon at that time and Villa was making things so hot that I concluded to get out if possible to the States, but I only got as far as Monterey, where I met a student at one of the colleges, who offered to get me a piece of sheet nickel from the college laboratory.

I finally completed my apparatus, which consisted of a small tank that could be heated externally. In the bottom of the tank I fastened the piece of sheet nickel. Resting on the nickel was a carpenter's oilstone which could be turned by a shaft

\*A paper read at the St. Louis meeting of the American Chemical Society, April, 1920, Division of Industrial Chemists and Chemical Engineers, and published by permission of the Society.



that passed through the top of the tank. There were the necessary valves for oil and hydrogen, etc. With this crude apparatus I made four or five trials, using about 3 gal. of cottonseed oil before I got things in shape and the apparatus tight. The last trial I made with this apparatus, I think, I had a peon turning the crank that actuated the stone and watching the temperature, while another was attending the gas producer. I think I kept this going three days, as the oil was getting darker each day from the fine nickel that was present, and when the sample of the third day cooked down I was sure that the oil had apparently hardened somewhat.

The next day Carranza attacked the town and my little laboratory was burned down, but several days later I removed some of the wreckage and secured some of the oil from the tank, and then I knew for sure that I had done some work.

Shortly afterward I returned to the States, and it was while I was working for the Allbright-Neal Co. that I mentioned to W. B. Allbright my experiences in trying to produce a nickel catalyzer mechanically. Mr. Allbright offered to finance me if I would continue the line of investigation and I accepted his very kind offer.

After several months trying all kinds of abrasives, I suddenly remembered the black oil from the journal box, and it was not long before I was grinding a mixture of oil and finely ground quartz. After several trials I was sure that I was on the right track. I next secured a sheet of nickel about 12 in. square and with a piece of old anode for a rubber or scrubber I was able to produce a catalyzer that would harden cottonseed oil in five or six hours.

During all this time I was greatly encouraged by the cheerfulness of Mr. Albright, and many very interesting experiments that he suggested were carried out. I think he suggested to me to use an ordinary closed tumbler or tube mill filled with grain nickel, oil and finely ground quartz. In the tumbler we tried out an atmosphere of hydrogen, also carbon dioxide.

There were some features about the catalyzer that we did not fully understand, and at this stage of the game we applied to W. D. Richardson, chief chemist of Swift & Co., to assist in putting on the finishing touches and rounding off the corners that had troubled us so sorely towards the end.

The time I spent with Mr. Richardson and his assistants satisfied me that they were as enthusiastic as Mr. Allbright and myself regarding the possibilities of a mechanically produced catalyzer, and especially was I satisfied that what I had set out to do had been accomplished.

At this point I should like to make a few observations in retrospect upon the Elder process. In the first place, you will notice that Mr. Elder had the courage of his convictions, which the great majority of chemists have not. We have been talking for years about finely divided nickel and other metals as catalysts, but no one before Mr. Elder had the sagacity and courage to prepare finely divided nickel by the simplest and most practical means. In short, we have all talked about finely divided nickel and finely divided metals as catalysts, but did not produce catalysts in the way suggested by our words, namely, by taking bulk metal and subjecting it to a process which would actually finely divide it in the precise meaning of those words. On the contrary, our so-called finely divided catalyzers have been produced in the past by a reduction in a chemical way of metallic salts, oxides and other compounds.

As a second observation, it appears after Mr. Elder's invention that whenever anyone of us took the trouble to whet his pocket-knife upon an oilstone he produced catalytic material, in this case catalytic iron, and furthermore, that all used lubricating oils which have been used to lubricate the surfaces of iron and more noble metals contain after a period of time finely divided catalytic material, although probably in most cases contaminated by carbon, sulphur and other substances sufficient to reduce the catalytic activity by a considerable amount.

Mr. Elder used the catalytic nickel prepared by him with the simple apparatus I have described to hydrogenize cottonseed oil in a laboratory way. The catalytic material produced in this small apparatus consisted naturally of a suspension of the finely divided metallic catalyst in oil, together with a certain amount of the abrasive. The longer the rubbing or abrading process was continued, the greater would be the relative portion of metal contained in the suspension. If the abrasive action was continued for a short time only, then the abrasive would predominate in the mixture. Mr. Elder also prepared catalyzer in dry form by abrading nickel surfaces with a suitable dry abrasive in the absence of oil. This catalyzer was found to be active, but not as active as catalyzer prepared in oil.

#### GRINDING WITH COUNTER ROTATING DISKS

Naturally the amount of catalyst which could be produced by man power applied to Mr. Elder's first apparatus within a reasonable length of time was very small, and hence Mr. Elder approached Mr. Allbright with the view of making arrangements for working upon a larger scale. With this end in view an apparatus was made consisting of two disks of nickel made to rotate in opposite directions

by mechanical means and to the opposed surfaces of which hot oil could be supplied. The friction of one plate upon the other caused finely divided nickel to be rubbed off into the oil and thus catalytic material was produced, but the amount was too small within a reasonable length of time to make this method of production a practical one.

#### TUBE MILL WITH NICKEL SHOT

As a further step a cast-iron tumbling mill was then made in which nickel shot was placed, together with a suitable abrasive and oil, and the entire mill rotated until a sufficient amount of catalytic material was obtained. This cast-iron mill was of a special shape designed to give maximum abrasion. It measured about 3 ft. in diameter and was 2 ft. long, measured along the shaft. It was soon found that the cast-iron mill did not produce the most desirable catalyzer for the reason that the abrasive acted not only upon the nickel shot contained in the mill but upon the sides and surfaces of the mill itself to such an extent that the final catalyzer obtained might contain as much as 60 parts of cast iron and carbon derived therefrom to 40 parts of nickel. This was the extent of the development of Mr. Elder's process as carried on by W. B. Allbright working with Mr. Elder in the plant of the Allbright-Nell Co., Chicago. The process was then turned over to the writer for further development in the Swift & Co. laboratories and plant.

After preliminary trials in the laboratory with small porcelain pebble mills, larger tumbling or pebble mills of the Abbé type were installed and these, in order to avoid contamination by iron admixture, were lined with porcelain brick. These mills measured about 5 ft. in diameter by 5 ft. long and were capable of holding a considerable charge of nickel shot.

#### SEVERAL TYPES OF ABRASIVES TRIED

In the laboratory and also in the larger mills all sorts of abrasives were tried—ground quartz of various mesh, ground pumice, carborundum, alundum, diatomaceous earth, etc. It was even found that a first-class catalyzer could be obtained with no abrasive at all, the friction of nickel shot on nickel finally resulting in the production of excellent catalytic material. During the course of the tumbling it was to be expected that a certain amount of the porcelain lining would become abraded and mixed with the catalytic material and abrasive. This admixture was not harmful to the catalytic activity of the finely divided metal, but from time to time the mills had to be relined. No attempt was made to separate the catalytic metal from the admixed abrasive. Many batches of oil were hydrogenized with the catalytic material just as it was removed from the mills and no adverse results were

experienced from the presence of the abrasive or abraded mill lining. Mechanical catalyzer was prepared by the Elder process both in the presence of air and of hydrogen and no great practical difference in activity in the two cases resulted.

Since a semi-drying oil was generally used in the mill, any atmospheric oxygen in the mill was usually absorbed by the oil during the course of the run, so that by far the greater portion of the catalytic material was actually prepared in the presence of nitrogen only, in this case. One other method of preparation, namely, by grinding in the presence of water instead of in the presence of oil, was made use of, and this produced a more active catalyzer, as will be described further on after a consideration of the original Elder catalyzer ground in oil.

#### A NICKEL MILL

An ideal mill for the preparation of metallic catalyzer by abrasion would be constructed with a lining of the same kind of metal as the charge and the desired catalyzer. For the preparation of nickel catalyzer, the lining of the mill would consist of nickel plates, preferably of sufficient thickness so that they could be wedged into place against the circular periphery of the mill. The side plates would have to be screwed or bolted on, and if thinner plates were used, these plates would naturally have to be screwed or bolted to the casing at all surfaces. Such a mill would undoubtedly produce a very much larger yield of active catalyzer than a porcelain-lined mill and would have the further advantage of avoiding additional contamination of silica or silicates from the lining. Although this contamination does not injuriously affect the catalyzer, it necessarily does dilute it beyond the dilution which would be determined by the introduced abrasive alone. The metallic linings would have to be replaced from time to time when they were worn too thin, but there would be no loss of nickel, since the removed plates could be cut into small cubes or melted into shot and reintroduced as part of the charge.

#### THE ELDER NICKEL CATALYZER

Under the microscope the Elder catalyzer is seen to consist of minute, opaque metallic particles usually but not invariably characterized by straight line edges and sharp angles. They are of various sizes, depending on the abrasive used and the length of time used in their preparation. Often they appear to be in the form of thin plates and some of them remain unattached, while others clump themselves into groups or lines. The particles have a distinctly metallic appearance as contrasted with the translucent or transparent appearance of some chemically prepared catalyzers of extremely high activity.



In activity the Elder catalyzer ranks very high, and this apparently can be increased indefinitely by long-continued abrasion. It is obvious, however, that there is a practical time limit to the operation and under ordinary operating conditions this cannot with economy be exceeded. It varies according to the type of mill used, the abrasive used, the amount of oil used, etc. It can be made to approach very closely to chemical catalyzer of the highest activity, although it is probable that chemical methods produce somewhat more active catalyzer under practical working conditions than that capable of being produced mechanically. However, it is very much superior to slow-acting chemically prepared metallic catalyzer and to much of the catalyzer that has been used in the past regularly for hydrogenation as well as for other purposes.

#### ACTION OF MECHANICALLY PREPARED NICKEL CATALYZER

The action of mechanically prepared nickel catalyzer in the hydrogenation of oils is somewhat different from that of other catalyzers of the same activity. The chemically prepared catalyzers for the most part when introduced into an oil in the presence of hydrogen show almost their highest activity at the start, that is, they may increase in activity by a small amount only, before the activity curve begins to fall. As contrasted with this form of curve, the Elder catalyzer activity curve shows a considerable rise at the commencement of hydrogenation which may last for some time before the curve reaches its peak and begins to decline.

The catalyzer can be used over and over a number of times like other active catalyzer. The usual method of recovery for re-use is by means of filter pressing. In the case of highly refined edible oils, the catalyzer may be recovered and used again for from five to ten or even twenty runs; in the case of lower grade oils, the catalyzer is killed after a much shorter period of use in the same manner as other metallic catalyzers and doubtless by the same means. There always seems to be a noticeable amount of combined sulphur present in dead catalyzers, and without doubt sulphur is one of the active poisoning agents.

The final recovery of the nickel catalyzer made by the Elder process is by means of fusion in a small oil- or gas-fired furnace. The filter pressed catalyzer with its attendant abrasive is first freed of fat by extraction or by burning, then mixed with a suitable flux and introduced into the furnace. The nickel becomes molten and can be recovered in the form of shot by running into water in the usual manner.

The fact that the abraded portions of the bulk nickel or nickel shot consist of catalytic

material naturally suggests as a corollary that the abraded surfaces of the nickel shot or bulk nickel itself are also catalytic, and this is the fact. The shot, therefore, after abrasion, could be used for hydrogenation in a hydrogenation tower and could be reactivated by the very simple process of removal from the tower and introduction into the abrasion mill.

#### SIMULTANEOUS GRINDING AND HYDROGENATING

Mr. Elder, in one of his patents, describes another ingenious application of his process. He maintains the catalytic material in a state of continued activity by conducting the hydrogenation process in the abrasion mill itself. Under such circumstances a continuous supply of active catalytic material is afforded and the activity of the catalyzer therefore cannot run down. The rate of chemical action is limited only according to the law of mass action and not by the poisoning of the catalyzer. I do not mean to suggest by this that poisoning does not occur, but only that it is not effective, inasmuch as a fresh supply of active catalytic material is continuously furnished.

#### SCIENTIFIC ASPECTS OF ABRADED NICKEL CATALYST

The type of catalyzer which I have described is not only of the greatest interest and importance in a practical way for the hydrogenation of oils and for other industrial catalytic reactions, but may be considered perhaps even more important for the theory of catalysis. That theory, particularly wherein it deals with metallic catalyzers, has emphasized the fact that the catalytic action was a surface action and presumably proportionally to the total surface of the catalytic metal or metal particles. Nevertheless, in the past metallic catalysts have been made universally by chemical means and while it was known that when obtained, the extent of the surface was to a large degree beyond control and it would have been difficult working by chemical means to obtain catalysts consisting of graded particles of different sizes and with different ratios of surface to mass. By the abrasion method catalysts of every degree of activity can readily be obtained from coarse, slowly acting catalysts to those of the utmost fineness, surface extension and activity.

Another point of the greatest interest is the fact that when the abrasion method is used there can be no doubt about the metallic character of the product. In the case of nickel catalyzer designed for hydrogenation and prepared by the chemical methods, it has been claimed by one school of theorists that the active particles do not consist of metallic nickel but of a sub-oxide of nickel and that in the

true metallic condition finely divided nickel is unsuited for the purpose of hydrogenation.

The abrasion method for preparing nickel catalyst proves beyond question that finely divided metallic nickel obtained from bulk nickel by purely mechanical means is an active catalyst for the hydrogenation of oils and other hydrogenation reactions. The nickel particles so prepared (as described above) are decidedly opaque and metallic in appearance under the microscope. They also become decidedly magnetic when placed in a magnetic field and thereafter tend to group themselves end to end in chains as might be expected, while, under the influence of a bar or horseshoe magnet, the particles group themselves along the Faraday lines of force as do iron filings.

#### EFFECT OF TEMPERATURE ON THE ACTIVITY OF METALLIC CATALYZER

The statement has been made and reiterated in the chemical literature that nickel catalyst must be prepared at a low temperature to be active, the temperature favored for the reduction of nickel oxide, for example, being about 300 deg. C. and preferably lower if effective reduction conditions can be maintained at a lower temperature. The facts in the case of chemically prepared reduced catalyzer are well established. If high temperatures are used for the production of such catalyzer, an inactive product is obtained, but the underlying assumption that heat treatment in and of itself must of necessity produce an inactive catalyst appears unwarranted in the light shed by Mr. Elder's discovery. The nickel shot or the nickel plates used for the production of this catalyst have been subjected to a temperature above the melting point of nickel, let us say above 1,470 deg. C. All of the catalyzer particles have been heated to this temperature, but it has not had the effect of deadening their activity. Our views, therefore, in regard to the effect of high temperatures on metallic catalyzers will have to be modified in conformity with these new facts established by mechanically prepared metallic catalyzers.

#### WATER-GROUND CATALYST MORE EFFECTIVE

I should like to conclude my paper at this point, having shown definitely and conclusively that nickel catalyzer prepared by the abrasion process and in the metallic condition and having been subjected to a high temperature is a decidedly active catalyst, but as a matter of fact, working in our laboratory and plant on the development of mechanically prepared catalyzers, we were able to produce a still more effective catalyst by substituting water in the abrasion mill for oil. Catalyzer prepared in the presence of water has the disadvantage of necessitating the removal of the water and the substitution of oil therefor prior to the

introduction of the catalyst into the hydrogenation apparatus or converter. This, however, was not especially difficult or expensive. The catalyzer produced in the presence of water was definitely, decidedly and invariably more active than that prepared by grinding in oil. Various explanations for this increased activity may be assumed:

1. That in the presence of water the abrading action produced a more finely divided catalyst.
2. That there would not likely be any catalyzer poisons in the water which might on the other hand be present in any oil produced.
3. That by grinding in water and in the presence of air a film of sub-oxide is formed on the catalyzer particles.

The last explanation may be the true one<sup>1</sup> and if so we are once more confronted with the importance of the sub-oxide theory and forced to conclude (if this explanation is correct) that while nickel in the metallic condition will catalyze hydrogenation reactions, nickel coated with a sub-oxide layer will catalyze at a still more active rate. However, a comparison should be made at this point between mechanical catalyzer prepared in water and by dry abrasive in air with no fluid medium present. In the last-mentioned case an active catalyzer was produced, but one much less active than the two other types mentioned. Apparently, therefore, too much oxidation during preparation is injurious, and if a sub-oxide film increases the activity of nickel catalyzer, this film must be kept within the narrowest limits if the most active type of catalyst is desired.

#### SUB-OXIDE THEORY

In considering the sub-oxide or oxygen-layer theory, it should be remembered and emphasized that we are dealing with a hydrogen reaction and that to bring this reaction about, the catalyst, whether nickel or palladium or other metal, must have, or does have, large volumes of hydrogen occluded on its surface and below the surface. It is difficult to believe that any oxygen or oxide could long persist under this condition and at the relatively high temperature employed in hydrogenation, but on the other hand, the reduction of the oxide or oxygen-layer might result in an increase of surface by roughening or furrowing, and if this hypothesis is correct, metallic nickel would still be the active agent, a larger surface having been obtained by alternate oxidation and reduction. Again, the oxygen might have the effect of offsetting the influence of certain poisons such as sulphur (sulphides),

<sup>1</sup>In this connection compare Rupert: "The Effect of Surface Oxidation on Some Metallic Catalyzers." *J. Am. Chem. Soc.*, vol. 42, p. 402, March, 1920. References to the previous literature are given.



which when exposed would not again be reduced under the conditions of the reaction, as is well known. Sulphates, such as calcium sulphate, sodium sulphate, nickel sulphate, etc., have been found to be quite without adverse effect or any effect at all in the hydrogenation of oils.

#### CONCLUSION

In this paper I have not attempted to give a complete exposition of the preparation of metallic catalyzers by mechanical means, but only to touch upon the more important points.

They are comparatively new in industry and have not as yet had the widest use. They must commend themselves for the simplicity, certainty and directness of their preparation and for their necessary uniformity. They will undoubtedly prove useful in developing the theory of catalytic activity.

In conclusion, acknowledgment is made to Paul Escher and G. W. Phelps of the Swift & Co. laboratory force for assistance in developing the catalyzer.

Laboratory of Swift & Co.,  
Chicago, Ill.

## Synthetic Acetic Acid and Acetone

BY J. T. ROONEY

THE great war was responsible for very many interesting industrial developments in which chemistry played a leading part. The progress of hostilities created demands for some materials greatly in excess of their previous rate of production or even any preconceived ideas of war-time necessity.

The extravagant use of artillery by the British on the western front, using cordite as a propellant, required a great quantity of acetone for the manufacture of this explosive, and it was soon discovered that the supply obtainable from wood distillation was entirely inadequate and new possible sources of manufacture were eagerly sought.

Necessity is said to be the mother of invention and to know no law, and so the urgent demands of war gave birth to many new ideas and fostered many new developments. The manufacture of acetone was undertaken from a variety of new sources, including calcium carbide, molasses, kelp, grain, etc., with varying degrees of success. Probably the most interesting, from a chemical point of view, is that including the synthesis of acetic acid from calcium carbide, water and air.

The various steps in this process had been the subject of much research and several patents before the war, but little had been done up to that time on its commercial development. Subsequent events, however, provided a stimulus which resulted in the synthetic production of great quantities of alcohol, acetic acid and acetone in America, France, Switzerland and Germany.

The Shawinigan Water & Power Co. of Montreal, Canada, which controls a large power development and calcium carbide plant at Shawinigan Falls, was approached by the British War Ministry on the possibility of producing acetone synthetically at Shawinigan

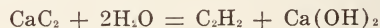
Falls. The result was that a subsidiary company called the Canadian Electro-Products was incorporated, and, after six months of research by the staff of the new organization, construction was begun and in the following eight months a \$2,000,000 plant covering fifteen acres was completed and working to capacity. The plant buildings are of brick, steel and fire-proof construction throughout, the floors being of concrete and metal lath and the stairways of iron.

Early in 1918, the Imperial Munitions Board, owing to the great need for acetic acid in the manufacture of cellulose acetate for aeroplane construction, instructed the company to discontinue the production of acetone and to confine its efforts to making acetic acid only.

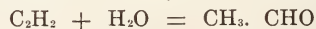
#### REACTIONS OF THE PROCESS

The synthesis of acetone takes place in four steps:

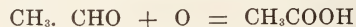
The production of acetylene from calcium carbide.



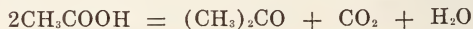
The hydration of acetylene to acetaldehyde.



The oxidation of acetaldehyde to acetic acid.



The formation of acetone from acetic acid.



#### DEVELOPMENT OF THE PROCESS

After the nature and extent of the reactions involved in the various steps of the process had been thoroughly investigated in the laboratory, a small building was allotted for an experimental plant, and in this development proceeded on a semi-commercial scale. It was at this stage that most of the difficulties were

encountered and overcome. One of the first problems was the selection of a suitable material for a vessel which would withstand the action of weak sulphuric acid with metallic mercury, and it was found that an acid-resisting silicon-iron was the only satisfactory medium.

Another problem which had to be solved early in the game was the preparation of the yellow mercuric oxide, which acts as a catalyst in the conversion of acetylene to acetaldehyde. This material was required in considerable quantities, and the process of making it from nitric acid and metallic mercury with subsequent conversion of the nitrate to oxide by ignition would have proved a troublesome and costly process on a large scale and consequently new methods of preparation were sought. The process finally developed, and with which very excellent results were obtained, was the electrolytic oxidation, at the anode, of metallic mercury to the oxide, using caustic soda solution as an electrolyte.

Owing to the difficulty of obtaining air-liquefying apparatus for the separation of oxygen from the atmosphere, attention was directed to the utilization of air directly for the oxidation of acetaldehyde to acetic acid, and after many experiments with various metallic containers, numerous catalysts, etc., the task was successfully accomplished. It was found that the reaction could not be controlled in iron, copper, etc., owing to the catalytic action of these metals which was responsible for several explosions at this stage, and it was eventually decided that aluminum was the only metal which could be safely utilized in this capacity.

For the conversion of acetic acid to acetone, numerous experiments were made with oxides and carbonates of calcium, magnesium, barium, zinc, manganese, etc., to determine the most suitable catalyst for the reaction, and the best results were obtained by use of hydrated lime containing a little magnesia.

As in every chemical development, a very considerable amount of work was required to determine the best operating conditions for every step of the process.

#### PLANT EQUIPMENT AND OPERATION

The hydration of the acetylene to acetaldehyde is carried out in Duriron kettles, 4 ft. dia. x 12 ft. high, built in circular flanged sections clamped together. In operation, a kettle is filled with water to about three-quarters capacity and sulphuric acid added to make a 6 per cent solution, then mercuric oxide charged in at regular intervals while acetylene is introduced at the bottom of the kettle and allowed to percolate upward through the solution. The mercuric oxide is kept in suspension by the action of the entering gas and by

mechanical stirrers. These stirrers, three in number, have paddle blades perpendicular to the shafts, the latter extending to the bottom of the kettle, where they fit into guide sockets. Each stirrer shaft is supported from a collar at the upper end which revolves on ball bearings and is connected with bevel gears to a  $7\frac{1}{2}$ -hp. motor bolted to a framework on the top of the kettle. The relative weakness of acid-resisting silicon-iron made it impossible to construct these stirrers entirely of this material, and as no other metal was adaptable to the purpose, the difficulty was ingeniously surmounted by the use of a steel shaft over which were fitted sleeves of Duriron, cast in sections with paddles and held tightly together by means of a nut threaded on the shaft.

A rubber gasket between each two sleeve sections prevented leakage of acid to the inner shaft. The lower end of the steel shaft was threaded with an iron nut cast in a piece of Duriron, against which the lowest sleeve fitted tightly.

Acetylene gas is admitted into the bottom section of a kettle through a perforated Duriron pipe and rises through the solution, where it is partially converted into acetaldehyde, the unaltered portion passing out with the aldehyde vapor at the top of the kettle and through condensers and scrubbers into a gasometer, from which it is returned by a Nash hydro-turbine to the kettles. Additional acetylene is admitted to the system under pressure at the same rate as the gas is being converted. One charge is operated 50 hr., after which it is dumped and the acid and catalyst renewed. A temperature as nearly 70 deg. C. as possible is maintained in the kettle and the aldehyde, which is boiled off and condensed, runs to brine-cooled containers for storage.

In December, 1918, a disastrous explosion, evidently due to a leakage of acetylene or aldehyde with accidental ignition, wiped out the building in which this part of the process was carried out. Several lives were lost and considerable damage was done.

#### ACETALDEHYDE CONCENTRATION

Crude aldehyde (from the previous step of the process), a 35 per cent solution in water, is pumped from storage to the still house, where it is concentrated to 99 to 100 per cent and stored again in cooled wrought-iron containers. The motor-driven crude aldehyde pumps are controlled automatically by a float and trip-switch in a small supply tank at the top of the still-house. The equipment in this building consists of continuous stills and rectifying columns of cast iron with automatic steam control regulated by vapor tension in the columns. The outlet at the top of the columns is connected to condensers, which are in turn vented to the atmosphere. The addi-



tion of a little fine chalk to the crude aldehyde feed neutralized the acidity and added considerably to the life of the apparatus.

#### OXIDATION OF ACETALDEHYDE TO ACETIC ACID

Pure acetaldehyde, in charges of 1,000 gal., is pumped into heavy iron kettles lined with aluminum, in which the conversion to acetic acid takes place. This part of the process requires the most careful attention of any owing to the extreme sensitiveness of the reaction involved and the absolute necessity of the most

which returns liquid aldehyde through a seal to the bottom of the kettle.

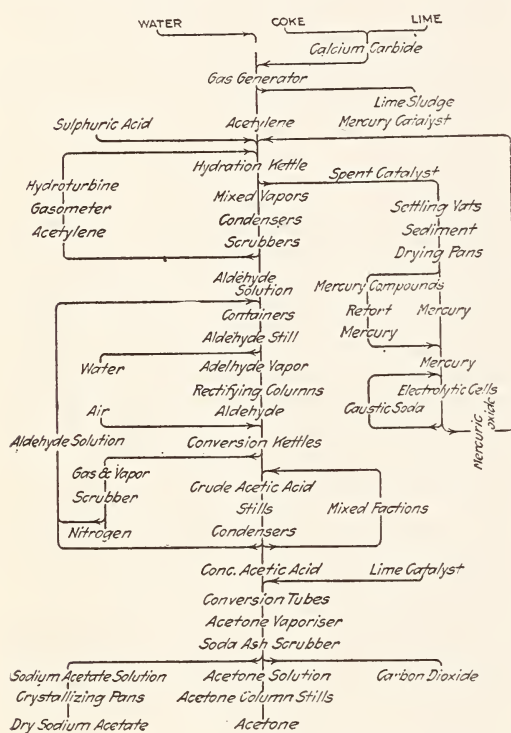
The outlet from the kettle is carefully restricted to the cracking of a valve during operation, and the gases which escape pass through a large scrubber, which collects in water any aldehyde that may be carried out with the escaping nitrogen. For safety in operation, each kettle is equipped with duplicate thermometers and pressure gages, which are watched constantly by the operator. There is put into one charge 1,000 gal. of aldehyde, and it requires about 12 hr. to reach an acidity of 95 per cent in terms of acetic acid. It is then considered finished and is dumped. So completely is the oxygen absorbed from the air in this operation that the scrubber gas content seldom exceeds 0.1 per cent. In spite of every precaution, fatal explosions and fires have occurred in this building.

#### ACETIC ACID REFINING

The crude acetic acid containing small amounts of aldehyde, manganese acetate, water, etc., is refined by fractional distillation in copper stills with aluminum fractionating columns, dephlegmators and condensers. The aldehyde fraction comes off first and goes to the aldehyde storage; mixed fractions are run with a subsequent charge. Water-white acetic acid, 99.8 per cent pure, is produced by this distillation.

#### PRODUCTION OF ACETONE

In this step of the process, vaporized acetic acid is passed through a heated tube containing a catalyst which effects the decomposition of acetic acid with the formation of acetone, the products passing through a hot scrubber containing soda ash, which converts the unaltered acetic acid into sodium acetate and allows the acetone to pass through into condensers, from which it is obtained in a 20 per cent solution. When this operation was tried on a large scale it was found that the larger conversion tube, measuring 12 in. dia. x 13 ft. in length, did not function so well as the experimental one which had been made from a 4-in. wrought-iron pipe. In the larger installation, steel tubes were used covered with asbestos and mica and wound with 290 ft. of No. 12 nichrome ribbon. The winding was made in several parallel circuits for convenience in temperature control. These tubes were packed with pumice on which the catalyst, hydrated lime, was deposited, but owing to the poor conductivity of the pumice it was impossible to maintain the required temperature of 485 deg. C. A central heating core was then added, but even this did not have the required effect, and the pumice was finally replaced with iron balls coated with lime.



FLOW SHEET OF PROCESS

accurate control. Manganese acetate, ground to 200 mesh, was found to be the most satisfactory catalyst for this reaction.

Air is admitted to the bottom of the kettle under high pressure, helping to keep the catalyst in suspension, and the oxygen is rapidly absorbed. The operation is carried out at a temperature of 60 deg. C. and under a pressure of 65 lb. per sq.in. in the kettle, the pressure being regulated by the rate of admission of high-pressure air and contraction of the outlet of the kettle. The temperature is kept down by circulation of cold water in coils inside the kettle. The dome of each kettle is connected with a set of reflux condensers,

Seventy-two such conversion tubes were installed, requiring 12 to 15 kw. each for heating, and these gave a daily production of ten tons of acetone of great purity with an operating efficiency of 85 per cent for the entire period of production. It was necessary, in this process, to renew the catalyst about every two weeks.

#### PREPARATION OF MERCURIC OXIDE

The yellow mercuric oxide catalyst used for the conversion of acetylene to acetaldehyde is prepared by the electrolysis of a caustic soda solution in circular castiron cells, 6 ft. dia. x 15 in. deep, having the inside walls lined with cement.

A layer of metallic mercury on the bottom of the cell serves as anode. A large sheet-iron cathode, like a spider web in appearance, is suspended below the surface of the electrolyte.

A stirrer revolves between the electrodes to remove the oxide formed from the surface of the mercury and to keep it in suspension. At the end of a run the oxide is washed from the cell with a hose and settled in vats, from which it is used directly in the wet condition. The caustic soda is used repeatedly.

#### RECOVERY OF MERCURY

The recovery of the mercury was another problem involving many difficulties and for which quite an extensive equipment was required. When a charge containing the spent catalyst is dumped from an acetylene conversion kettle it is settled in conical wooden vats, after which the supernatant liquid is siphoned off and passed through a series of settling tanks to catch all the mercury possible. The sediment remaining in the conical vats, consisting of metallic mercury, mercury compounds, etc., is then neutralized with soda ash and charged into covered, steam-jacketed drying pans fitted with stirrers and operated under a full vacuum. When the contents of these pans have been dried, metallic mercury is run off and the remaining material then charged with reducing agents into retorts for distillation. These retorts are oil-fired and the pots were at first made of cast iron, but this material had a very short life and the expense of renewal was excessively high, but later nichrome alloy pots were tried out and gave more efficient service in spite of the greater initial cost.

The extensive handling of mercury in the various steps of the process was the cause of much sickness until proper precautions had been studied and enforced.

#### A NOTABLE ACHIEVEMENT

This undertaking of the Shawinigan Water & Power Co. was a notable achievement, both from the point of view of the success attained and the remarkably short transitional period from the laboratory research stage to one of large-scale production. It is also a striking example of the major rôle played by chemistry in modern warfare and a proof that Canada did her "bit" in the laboratory as well as on the battlefield. The frequent necessity for use of the regulation army gas mask for protection against lachrimatory gases such as croton-aldehyde, etc., contact with the poisonous mercury catalyst and the ever-existent danger of explosion or fire presented a parallel for life in the trenches and a casualty list equally as deserving of an enduring place on the roll of honor.

When the United States Government entered the war and planned a huge aerial program, great quantities of acetic acid were required for manufacture of cellulose acetate varnish, and it was found expedient, by arrangement with the Shawinigan Water & Power Co., to duplicate, on the spot, the plant at Shawinigan Falls.

This new plant, called the American Electro-Products Co., was about completed and ready for operation when the armistice was signed. So well had the development of the process been carried out in the beginning that, even with the experience gained by a year's operation, only minor variations from the original design were found necessary in building the second plant. The combined plants have a capacity of more than fifty tons of glacial acetic acid per day.

#### CONCLUSION

The products of the various steps of the process form possible bases for the manufacture of an unlimited variety of valuable organic chemicals, and the apparatus, in excess of that required to supply a normal acetic acid demand, might readily be adapted to the manufacture of countless new products.

In cost of production, the synthetic process, when associated with the carbide industry, can at present about hold its own with the wood-distillation process and should ultimately entirely displace the latter.

Extensive research by a large staff is now being carried on in the well-equipped laboratories and experimental plant of the Canadian Electro-Products Co. and the company looks with every confidence to the future.



## Testing Natural Gas for Carbon Black

BY ROY O. NEAL\*

**B**EFORE work is begun on a plant for the production of carbon black from natural gas, the gas should be tested. The actual amounts of carbon black obtained by the same process when using different gas may vary decidedly, as is shown in Table 1. The quantity recovered closely follows the percentage of ethane<sup>1</sup>, heating value and amount of elementary carbon calculated from the hydrocarbons determined by analysis. The gas from Louisiana has the lowest percentage of nitrogen and the highest percentage of hydrocarbons, namely, 97.56, yet when burned at a factory it gives the smallest yield of carbon black. This is due to the large proportion of methane, which contains 33.5 lb. of carbon per thousand cu.ft., whereas ethane contains 67 lb. of carbon. The two gases from West Virginia have very similar compositions and give approximately the same yield of carbon black. The

as trustworthy an indication of the available carbon black as that obtained with a small portable apparatus where gas is burned and the deposited carbon black is collected and weighed.

The writer has designed an apparatus for determining the quantity of carbon black which one might expect to obtain from an unknown gas. Details of the apparatus are shown in Fig. 1. The apparatus is made of 16-gage sheet iron held together with  $\frac{3}{8}$ -in. rivets. The carbon black is deposited upon a plate  $8 \times 10\frac{3}{4} \times \frac{1}{4}$  in. and is removed by a scraper  $1 \times 8 \times \frac{1}{8}$  in. that is operated by hand. The draft is controlled by eight 1-in. ventilating holes provided with covers, which are pivoted above the holes, and by a revolving damper located at the top of the hood. The pipe carrying the lava tips can be lowered below the depositing plate and held at any distance by attaching a plug in stopper holes below the supports. The hopper carries a sliding door for removing the carbon black. Lava tips capable of burning about 4 cu.ft. of gas per hr. are used. The hood, hopper and legs are detachable and fit into the central portion of the device to facilitate transporting in the field. The apparatus can be used in the field by connecting directly to the supply of gas and using suitable wind breaks if assembled in the field, or can be used in the laboratory by obtaining a sample of gas under pressure in a steel cylinder.

The source of supply of gas is connected with a meter registering at least as small a quantity as one-tenth of a cu.ft. and on this line should be a quarter-inch needle valve in order to limit the flow of gas through the apparatus. Between the meter and the apparatus, where the gas is burned, is attached a "U" tube for determining the pressure of the gas. The top of the lava tips should be about  $2\frac{1}{2}$  in. below the depositing plate and a gas pressure of from  $\frac{1}{2}$  to 1 in. of water should be maintained. These factors will of necessity be changed when examining different gases and in the preliminary tests changes should be made until the largest recovery is obtained. A test should last at least an hour, during which time 15 or 20 cu.ft. of gas should be burned. It is possible to make a test without using the meter in the field by previously calibrating the apparatus against a meter in which different pressures on the manometer tube are observed and the time recorded. This will give fairly accurate data on volumes, provided, of course,

TABLE 1. CARBON CONTENT AND QUANTITY OF CARBON BLACK RECOVERED BY CHANNEL PROCESS

	Louisiana (a)	West Virginia (b)	West Virginia (c)	Wyoming (d)
	Per Cent	Per Cent	Per Cent	Per Cent
Methane <sup>1</sup> .....	94.12	70.75	65.23	46.45
Ethane.....	3.44	24.14	30.07	43.10
Carbon Dioxide..	0.50	0.28	1.56	0.96
Nitrogen.....	1.94	4.83	3.14	9.49
Heating value <sup>2</sup> ..	962	1,086	1,134	1,176
Lb. carbon per 1,000 cu.ft. of gas <sup>3</sup> .....	33.8	39.9	42.3	44.3
Reported obtained as carbon black, lb. per 1,000 cu.ft. ....	0.80	1.00	1.10	1.40
Per cent recovery	2.4	2.5	2.6	3.1

<sup>1</sup>Chemical analyses of gases were made by Donald B. Dow, junior chemist of Bartlesville Station, U. S. Bureau of Mines.

<sup>2</sup>Net heating value in B.t.u. per cu.ft. at 32 deg. F. and 760 mm. pressure.

<sup>3</sup>Calculated from carbon content of methane and ethane.

gas supplied to the plant in Wyoming has the largest calorific value, carbon content and considerably more ethane than any of the other gases and produces the greatest yield. With the richer gases not only the actual quantity of carbon obtained is larger, but also the per cent recovery increases. An examination of the chemical analysis of a gas is probably

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<sup>1</sup>For the chemical analysis of natural gas the reader is referred to "The Sampling and Examination of Mine Gases and Natural Gas," George A. Burrell and F. M. Seibert; Bulletin 42, Bureau of Mines, 1913. "Gas Analysis," L. M. Dennis, The MacMillan Co., New York, 1913.

that the lava tips are not broken, plugged, or partly restricted by foreign matter after the apparatus has been standardized. During the test the carbon black should be removed from the collecting plate by the scraper every 10 min., and at the end of test the carbon which

which one might expect to obtain in plant operation from a given gas can be calculated.

In both methods only comparative results are obtained. The portable apparatus will give results approximately paralleling those procured in commercial plants using the channel

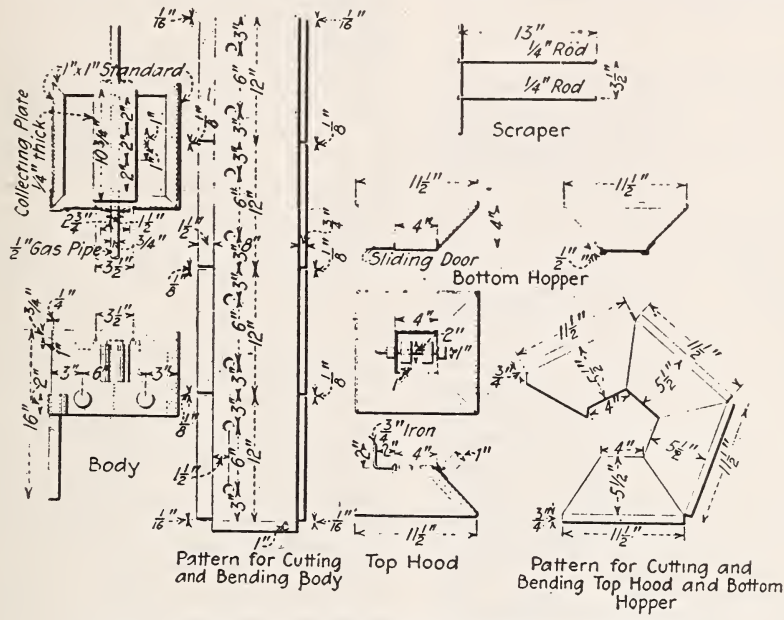


FIG. 1. DETAILS OF PORTABLE TESTING APPARATUS

is deposited on the sides of apparatus and plate is removed by use of a small brush. This accumulated carbon black is then weighed. From the data on the volume of gas burned, quantity of carbon black collected and pressure on the gas, the quantity of carbon black

system, but if some other process is used, it is necessary to standardize the apparatus against a plant where conditions will be similar to those where gas in question is examined.

White Oil Corp.,  
Tulsa, Okla.

# Inaccuracy of Treating Records Due to Moisture in Wood

BY ERNEST BATEMAN\*

IN STUDYING the effect of leaching on wood treated with inorganic salt preservatives, such as zinc chloride, copper sulphate, zinc sulphate, cresol-calcium, etc., it has frequently been noticed that the treating record did not check at all closely with the amount of salt found to be present in the wood. The treating record consisted in the weight of the piece before and after treatment, the difference between the two being con-

sidered as the amount of solution injected. This weight of solution multiplied by the per cent of concentration should give the amount of salt injected into the piece. Analysis of the wood after treatment frequently showed that there was often as much as 50 per cent more salt actually in the piece than the treating record showed should be the case and rarely if ever did the record and the analysis agree. In commercial practice the same phenomenon was noticed to a greater or less degree. The theory which has been advanced by wood pre-

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servers that there is a chemical union between zinc chloride and wood substance seems therefore to have some basis for its existence. If this is the case, then we must also attribute the increased absorption of such salts as zinc sulphate, copper sulphate, cresol-calcium, and as will be shown in this paper, calcium chloride, to the same cause.

#### EXPERIMENTAL DETERMINATION OF WOOD ABSORPTION OF INORGANIC SALT PRESERVATIVES

In order to throw some light on the subject small pieces of wood 2 x 2 x 8 in. were treated with zinc chloride solution and the solutions analyzed before and after treatment to determine if there was any change in the strength of solution. The amount of wood used was as great in proportion to the solutions as it was possible to make it. Three conditions of wood were used, oven dry, air dry, and green. The analysis of the solutions showed that there was a change in the strength of solution during treatment, but the weakening of the solution was not in proportion to the amount of wood present in the three runs, and in one case no weakening at all was obtained. The results were such that no very definite conclusion could be drawn. It was therefore decided to make a much more comprehensive and detailed study of the treatment, but in place of zinc chloride to use calcium chloride, chiefly because calcium is much more readily and accurately determined than zinc and at the same time it resembles zinc chloride in its solubility, deliquescence, etc. A small treating cylinder was used, and here again, as in the previous case, the amount of wood was made as large as possible in comparison with the treating solution. The weighed wood was treated to refusal at a temperature of 180 deg. F. Three conditions of wood were again used, oven dry, air dry, and green; the first containing no moisture, the second 15 to 20 per cent, while the third had 30 per cent or more. Actual moisture determinations were not made. The solution was weighed before and after treatment, separate solution being used for each run. As soon after treatment as possible the wood was removed from the treating cylinder and placed in covered glass jars to drip and cool. These were then weighed after cooling. The difference in weight before treatment and the weight after treatment and cooling was taken as the treating record. The drip and condensate were also weighed.

The wood was allowed to dry to some extent and was then reduced to sawdust and analyzed for calcium. The method of analysis consisted in ashing a weighed portion of sawdust and determining the calcium volumetrically by means of its oxalate. The accompanying tables show the results obtained.

TABLE I. TREATING RECORDS

	Run 1			Run 2			Run 3		
	Lb.	Lb.	Lb.	Lb.	Lb.	Lb.	Lb.	Lb.	
Wt. solution before treatment.....		21.90			21.60		20.90		
Wt. solution after treatment.....			16.53		16.07			15.77	
Wt. of wood after treatment.....	8.68			8.63		7.80			
Wt. of wood before treatment.....	4.09			4.80		5.29			
Absorption of sol. (by difference).....		4.59			3.83			2.51	
Drip.....		0.58			1.12			1.48	
Loss by leakage or evaporation.....		0.20			0.58			1.14	
		21.90	21.90		21.60	21.60		20.90	

TABLE II. ANALYTICAL RECORD

	Run No. 1		Run No. 2		Run No. 3	
	Strength Per Cent	Total Salt	Strength Per Cent	Total Salt	Strength Per Cent	Total Salt
Solution before treatment.....	1.84	0.4030	1.41	0.3046	1.79	0.3741
Solution after treatment.....	1.84	0.3042	1.35	0.2169	1.78	0.2806
Drip.....	1.35	0.0078	1.37	0.0152	1.61	0.0239
Found in wood.....		0.0873		0.0700		0.0695
Loss by difference.....		0.0037		0.0025		0.0000

#### CORRECTION OF RESULTS

Although an attempt was made in this work to reduce the losses of both solutions and salt to as small a factor as possible, in spite of these precautions small losses did occur. It is almost impossible to pump 20 lb. of solution from a carboy to a treating cylinder, put it under pressure, heat it to 180 deg. F., then after the completion of treatment release the pressure and catch all the solution, and entirely prevent evaporation either from the wood or solution or both. For this reason a complete audit of the solution and salt was made so that these discrepancies could be corrected.

The discrepancies which appear in this work must always be errors on the loss side and can be divided into two kinds:

1. Losses due to leaks and to transferring the solution,
2. Losses due to the evaporation of the solution because of its elevated temperature after treatment.

The former would cause a loss in both water and salt, the latter a loss of water only. Whenever we find that we have lost both water and salt in the same proportions, we are justified in assuming that this loss was due to a leak, and when we find that there was no loss of salt but a loss of water, we are justified in assuming that this loss was due entirely to evaporation either from the wood or from the solution. Where we have losses in both water and salt, but they do not check, then we can say that the loss of salt was due to leaks, while the loss of water in excess of this loss by leakage was due to evaporation.

#### RECORDS OF RUN No. 1

The amount of solution before treatment was 21.9 lb. That accounted for after treatment was 21.7 lb., or a loss of 0.2 lb. The

total amount of salt used was 0.4030 lb.; accounted for after treatment 0.3993 lb., or a loss of 0.0037 lb. The concentration of the solution before and after treatment was 1.84 per cent. A loss of 0.20 lb. by leakage would account for 0.0037 lb. of salt, or the actual

TABLE III. CORRECTED RECORDS OF RUN NO. 1

	Lb.	Lb.	Lb.
Wt. of sol. before treatment.....		21.70	
Wt. of sol. after treatment.....			16.53
Wt. of wood after treatment.....	8.83		
Wt. of wood before treatment.....	4.09		
Absorption of sol. by wood.....			4.74
Drip.....			0.43
		21.70	21.70
	Strength Per Cent	Total Salt	
Solution before treatment. ....	1.84	0.3993	
Solution after treatment.....	1.84		0.3042
Drip.....	1.84		0.0078
Found in wood.....			0.0873
		0.3993	0.3993

Salt in wood calculating from corrected treating record,  
0.0872 lb.  
Salt in wood found by analysis, 0.0873 lb.

loss found by experiment. We can therefore conclude that there was a small leak in the apparatus, which passed unnoticed during the run.

There was no change in the strength of the solution during treatment, nevertheless the drip solution is noticeably weaker than either of the solutions. At the same time there is more calcium chloride in the stick than ought to have been there if the treating record is correct. The sticks, after removal from the treating cylinder, were placed while still hot under a bell jar to drip. The steam arising from the wood condensed on the jar and ran down into the drip solution with a consequent weakening of this solution. The amount of this condensate can easily be calculated. The record shows 0.58 lb. of 1.35 per cent solution as drip. The weight of this solution must therefore have been increased by the amount of water necessary to dilute a 1.84 per cent solution to 1.35 per cent or

$$\frac{1.35}{1.84} \times 0.58 = 0.425$$

That is, the actual drip was 0.43 lb., the remaining 0.15 lb. being moisture which evaporated from the wood during cooling. This should be added to the treating record as being absorbed by the wood. The corrected record then reads as in Table III.

RECORDS OF RUN 3

In this run there was a loss of 0.89 lb. solution but no loss of salt. All the loss must therefore have been due to evaporation. This

may have taken place from the wood or from the solution. It does not seem likely in this run that much of this loss could have taken place from the wood because of the short time exposed after treatment. It is known, however, that the stopper was left out of the car-

TABLE IV—CORRECTED RECORDS OF RUN NO. 3

	Lb.	Lb.	Lb.
Wt. of solution before treatment...		20.90	
Wt. of solution after treatment....	7.87		16.91
Wt. of wood after treatment.....	5.29		
Wt. of wood before treatment.....			2.58
Wt. of drip solution.....			1.41
		20.90	20.90
	Strength Per Cent	Total Salt	
Solution before treatment.....	1.79	0.3741	
Solution after treatment.....	1.66		0.2806
Drip solution.....	1.66		0.0239
Found in wood.....			0.0695
			0.3740

Salt in wood from treating record..... 0.0462  
Salt in wood from analyses..... 0.0695  
Difference excess over treating record ..... 0.0233

boy for some time after the hot solution had been put into it, so it seems likely that the loss occurred at this place. If it all took place here, then the treating record of the solution after treating should be 16.91 lb. instead of 15.77, and the concentration should be 1.66 instead of 1.78. Here again the drip solution is weaker than the solution after treatment and if we follow the same line of reason-

ing we can correct this  $\frac{1.61}{1.69} \times 1.48 = 1.41$ .

Actual drip 1.48 — 1.41 = 0.07 due to evaporation. The corrected record then reads as in Table IV.

RECORDS OF RUN NO. 2

In this run we have both a loss of salt and a loss of solution. The loss of salt amounted to 0.0025 lb. or 0.18 lb. of 1.41 per cent solution. The remaining loss, 0.40 lb., must have been evaporation. It seems more than likely that most of this evaporation took place from the wood itself, because in treating the pieces became wedged in the small cylinder and considerable difficulty was experienced in removing them. Furthermore, the concentration of the drip is greater than that of the solution after treatment. This could only be obtained by evaporation of moisture from the wood and a consequent removal of the more concentrated solution by washing with the drip. This would of course take place chiefly at the ends and would account for only a small part of the actual loss, since the concentrated solution caused by evaporation from the sides would not



be removed by the drip. We are therefore justified in assuming that the loss by evaporation took place chiefly from the wood. On this

TABLE V. CORRECTED RECORDS OF RUN NO. 2

	Lb.	Lb.	Lb.
Wt. of solution before treatment...		21.42	
Wt. of solution after treatment....			16.07
Wt. of wood after treatment.....	9.01		
Wt. of wood before treatment.....	4.80		
Wt. of solution absorbed.....			4.21
Drip.....			1.14
		21.42	21.42
	Strength, Per Cent	Total Salt	
Solution before treatment.....	1.41	0.3020	
Solution after treatment.....	1.35		0.2169
Drip.....	1.35		0.0152
Found in wood.....			0.0700
		0.3020	0.3021
Salt in wood from treating record.....			0.0594
Salt in wood by analysis.....			0.0700
Excess over treating record.....			0.0106

basis the corrected treating records are as shown in Table V.

#### DISCUSSION OF RESULTS

Table VI summarizes all the important corrected data in the three runs.

In only one of these conditions does the treating record agree with the amount found by analysis, that is, the oven dry pieces. In

TABLE VI. SUMMARY OF CORRECTED DATA

	Oven Dry	Air Dry	Green
Wt. of wood, lb.....	4.09	4.80	5.29
Amount of solution used, lb.....	21.70	21.42	20.90
Strength of solution before treatment, per cent.....	1.84	1.41	1.79
Strength of solution after treatment, per cent.....	1.84	1.35	1.66
Change in strength of solution due to treatment, per cent.....	0.00	0.06	0.13
Amount of salt injected:			
By analyses of wood.....	0.0873	0.0700	0.0695
By treating record.....	0.0872	0.0594	0.0462
Excess injected over T. R.....	0.0001	0.0106	0.0233

this also the strength of the solution remained unchanged as a result of treatment. If there is any change in the concentration due to chemical affinity it ought also to be shown in this as well as in the two other cases. We can therefore discard the theory that the wood substances enter into a firm chemical union with the materials used in treating.

There is, however, a striking relation between the reduction in concentration of the treating solution, the apparent excess absorption of salt and the moisture content of the wood. With an increasing moisture content of the wood, the difference in concentration

of the solutions before and after increases, and the excess salt found in the wood increases.

This leads to the conclusion that the moisture present in the wood acts as if it had actually been added to the solution and decreases its strength. In other words, the water present in the wood is replaced by solution. This solution would then escape measurement because an equal amount of water takes its place. The amounts of water necessary to cause the reduction in strength for the two solutions are respectively 0.85 lb. and 1.69 lb. Unfortunately, moisture determinations were not made, but the treatments were made with the same number of pieces of approximately the same dimension and same species, consequently the oven dry weight of all three runs should be approximately the same. We should be able to form some idea as to whether or not there could be present in the wood sufficient moisture to cause the phenomena noted. If we take the oven dry sticks as a basis of oven dry weight, we find that there was at least 0.71 lb. water in the air dry stick and 1.20 lb. water in the green stick, so that it is not unreasonable to suppose that the difference between these weights and that required may be due to shrinkage of wood, differences in density of wood substance, and differences in the size of the pieces. If we then subtract the amount of water required to dilute the solutions from the green weight of the wood before treatment, we should get the dry weight of the wood.

$$4.80 - 0.85 = 3.95 \text{ lb.}$$

$$5.29 - 1.64 = 3.65 \text{ lb.}$$

Subtracting these weights from the weight after treatment should give us the amount of diluted solution into the wood.

Run No. 2	Runo. 3
9.01	7.87
3.95	3.65
5.06 of 1.35 per cent	4.22 lb. of 1.66 per cent sol.

on a salt absorption of 0.0684 and 0.0701 respectively, actually found by analysis being 0.0700 and 0.0695 respectively. From this it would seem that the correct explanation of the phenomena noted is that the water in the wood acts as a diluent of the treating solution and gives a greater treatment than is apparent from the treating record.

#### CONCLUSIONS

The following conclusions can be drawn from this work:

a. There is no apparent reason to suppose that a chemical combination results from the treatment of wood with most inorganic salts, such as zinc chloride, zinc sulphate, sodium fluoride, calcium chloride, etc.

b. The moisture present in the wood at the

time of treatment acts as diluent of the solution.

c. Any system of measuring the absorption of salt by wood during treatment which is based on a measurement of the weight or volume of the solution before and after treatment is liable to a very considerable error.

Only when the wood is free from moisture are such measurements exact. At all other times either weight or volume measurements will be in error because of the exchange of the moisture in the wood for solution so that more solution will actually be injected than is made apparent from the treating records.

## The Eventual Retort Plant for the Distillation of Oil Shales

By LOUIS SIMPSON

IN THE Aug. 15, 1919, issue of this journal, in an article treating upon Oil Shales and upon the Scotch Dual Purpose Retort, the principles that underlie successful retorting have been discussed at length.<sup>1</sup> In the Jan. 7, 1920, issue the question as to where it is commercially desirable to recover the nitrogen content of these shales has been answered.<sup>2</sup> It seems probable that many of those interested in the exploitation of oil-yielding shales have by this time arrived at the conclusion that the Scotch dual purpose retort is not the most economical retort possible to construct and operate for the eduction of the oil gases. Yet owing to certain qualities of shale containing by-products which it is desirable to recover because of the large quantity present or from local conditions that make their recovery profitable, it is necessary to consider the construction of a plant specially adapted for the recovery of one or more of such by-products as may be found in the spent shale. For those with such a problem this article is written.

It is probably admitted by those who seek the truth and who possess an unbiased mind that the most efficient retort for generating oil gases will be one specially designed for that purpose, without having regard to the recovery of nitrogen or of any of the possible by-products. The present problem to be considered therefore is how best to recover such by-products from the spent shale, that is, from the shale as it leaves the retort after the oil gases have been driven off.

### SUGGESTION THAT TWO MACHINES BE USED

There seems to be no special reason other than that it has been a matter of convenience that the recovery of the oil gases and the recovery of the nitrogen should have been attempted on one and the same machine, even if essayed in different sections of the machine. This convenience seems to have existed in the

method adopted for heating the Scotch dual purpose retort, but herein is found the great weakness of the retort.

The Scotch designers of the retort had a glimmering of the situation. They knew that the temperatures created by the combustion of the fuel used, whether solid or gaseous, were too high for the best evolution of oil gas, and so arranged to use the higher range of temperatures available for the recovery of the nitrogen, using the lower range for the eduction of the oil gases. This seemed to be a satisfactory solution of the difficulty, but in truth they placed themselves between the horns of a dilemma. If that section of the retort in which the nitrogen gases are driven off as ammonia gas was subjected to the comparatively high temperatures required, that section of the retort was soon put out of commission, and further provided a temperature far too high for satisfactory eduction of the oil gases in the other section of the retort. With such comparative high temperatures, the hydrocarbons were cracked, with the result that permanent gas was formed and the yield of oil was reduced. If, on the other hand, the temperature in the nitrogen recovery section be reduced to the safety point, so that the retort may not be burned out too quickly, then the recovery of nitrogen is very much less than the maximum possible.

Another point will be evident to the careful thinkers, viz., that the shale when it is passed to that section of the retort in which the recovery of the contained nitrogen is attempted is not in the best physical condition to give a maximum recovery, nor is it so placed, within the section, that each and every particle of the shale is submitted to the like high temperature. That disabilities exist is evidenced from the recoveries obtained, which do not exceed and usually fall under 60 per cent of the content.

Under these conditions it is surely evident that it is not possible to secure from the shale

<sup>1</sup>CHEM. & MET. ENG., vol. 21, No. 4, p. 176.

<sup>2</sup>CHEM. & MET. ENG., vol. 22, No. 1, p. 20.



an economical extraction of the by-products, after the oil gases had been driven off, in the Scotch dual retort and that such extraction should take place in a machine especially designed for the purpose and constructed so as to withstand the necessary high temperatures.

#### REQUIREMENTS OF MACHINE TO EXTRACT BY-PRODUCTS

The requirements of such a machine would be:

1. Capability of withstanding the comparative high temperatures necessary, without breaking down.
2. Every particle of shale under treatment must be subjected to the same heat treatment.
3. The spent shale, when under treatment, should be in a very finely disintegrated condition.

To obtain economically the high temperatures necessary, to provide that every particle of the shale shall receive the like heat treatment, the method of heating the spent shale has to be radically different from that used in the Scotch retort, and seeing that, at this stage, the shale has been freed from its hydrocarbon contents, there has ceased to be any reason why the shale should not be subjected to heat, *directly applied*, instead of as in the Scotch retort, *indirectly applied*.

Fortunately it is not necessary to invent any new machinery to meet the requirements of the case. The horizontal revolving kiln, so long and successfully used in the manufacture of portland cement to burn the "mix" into cement clinker, which is a perfected machine, seems to be peculiarly adapted for the work to be done.

In the manufacture of portland cement the "mix" (generally a mixture of clay and lime), finely ground, is subjected to temperatures of 1550 deg. C. (2820 deg. F.) and over. In the Scotch dual retort, the shale in the nitrogen recovery section is supposed to be exposed to a temperature somewhat around 1600 deg. F., but as there must be a great variation in the temperatures next to the walls of the retort and in those found in the center of the retort, it is difficult to ascertain just what temperatures are used. It is, however, now known that to obtain the recovery of the maximum yield of nitrogen as ammonia gas, every particle of the spent shale should be exposed to a temperature of 1125 deg. C., or 2060 deg. F. It is also known that a decrease of comparatively few degrees of temperature will result in a very large and entirely disproportionate decrease in the field, while an increase in temperature over the critical temperature increases the yield only slightly.

#### HORIZONTAL REVOLVING KILN TO HANDLE SPENT SHALE

It will be noticed the critical temperature for the recovery of nitrogen as ammonia gas is between the temperature required for the burning of cement clinker and the temperatures now found in the nitrogen recovery section of the Scotch dual purpose retort. It is therefore evident that the horizontal revolving kiln, as constructed for the burning of cement clinker, will be capable of handling spent shale.

#### FIXED CARBON IN SPENT SHALES

In all spent shale there remains some fixed carbon. This fixed carbon content may be as low as 2 per cent and as high as 25 per cent of the original shale. The quantity present in the spent shale will depend upon the treatment received by the shale during the process of distillation, and it must not be forgotten that during the distillation the weight of the shale is considerably reduced, the amount of reduction depending upon the richness of the shale. The percentage of fixed carbon in the spent shale will in most cases be largely increased, especially when the shale is rich.

To illustrate, certain shales upon analysis were found to contain fixed carbon in the following amounts: No. 1, 8 per cent; No. 2, 5½ per cent; No. 3, 2¼ per cent. If through distillation no fixed carbon be lost, the spent shale would contain: No. 1, 12¾ per cent; No. 2, 8 per cent, and No. 3, only 3¼ per cent. The difference is of importance, because while it is evident that some shale may contain sufficient fixed carbon to produce, by itself, upon combustion, the temperatures required, other spent shales do not, and in such case the carbon in the shale will have to be supplemented by powdered coal, fuel oil, or gas. The question of fuel, therefore, may be in some cases the determining factor as to whether it would be profitable to recover by-products from the spent shale.

#### PROBABILITY OF PRODUCTION OF INCREASED QUANTITIES OF AMMONIA GASES

It would appear probable that spent shale burned at the correct temperature, in a horizontal revolving kiln, in the presence of low pressure superheated steam, will produce largely increased quantities of ammonia gases, and that such increase may exceed one-third of the present yields. The production will be helped by the fine crushing of the spent shale before burning, and this can be done at a low cost, because the spent shale possesses physical characteristics which will permit of its being easily crushed so that 98 per cent will pass through a 200 mesh, as is done with the "dry mix" from which portland cement is made. It should also be noted that with this

preliminary crushing, and by the use of the kiln at the temperatures stated, it becomes possible to recover any potash that may be in the shale. When potash recovery is desired it may be necessary to increase the temperature, because it is stated (see pag 130, R. K. Meade's "Portland Cement") that the whole of the volatile contents of the "dry mix" is "not driven off until the clinker is completely burned and about to leave the kiln," and that then less than 1 per cent remains. From this it is evident that for potash recovery a high temperature within the kiln is essential. It is fortunate that the high temperature so required will not interfere with the recovery of nitrogen.

#### OPPORTUNITY FOR PIONEER WORK ON POTASH IN SHALES

It is known that potash in economic quantities has been found present in some shales, but it has not been ascertained whether its presence is universal or even if, when its presence has been discovered, it persists throughout the bed of shales in which it has been found. Much useful pioneer work might be done in this connection, now that an economical method of recovery is available.

#### METHOD FOR RECOVERY OF POTASH

The *modus operandi* for the complete process is as follows:

1. Eduction of oil contents of shale in retort expressly designed for that purpose.
2. Grinding of the spent shale so that 98 per cent will pass through a 200 mesh.
3. The ground spent shale is burned in a horizontal revolving kiln into which low pressure superheated steam is suitably introduced, the burning being obtained by the combustion of the contained carbon, supplemented, when required, by powdered coal, fuel oil, or fuel gas, but preferably fuel gas.
4. The fumes driven off are passed through a Cottrell dry separator, in which the dust and also certain portions of the potash are removed.
5. The fumes then pass through a specially constructed waste heat steam boiler, the product of which is low pressure steam, most of which is used in the kiln.

6. The fumes then pass to scrubbers, in which machines the remainder of the potash and the ammonia are recovered. The water from the scrubbers containing the potash and the ammonia is then treated with sulphuric acid, producing a salt which would make a very valuable chemical fertilizer.

#### PRODUCT IS A CONCENTRATED FERTILIZER

Though commercial mixed fertilizers are looked upon with disfavor by many, the above-mentioned mixture need not necessarily come under such strictures. As a concentrated fertilizer, in a form that is readily soluble, it would have much to commend its use.

It need hardly be pointed out that the Scotch dual purpose retort cannot provide the temperatures necessary either for a full recovery of the nitrogen or for the recovery of such potash as may be found, in commercial quantities, in some shales.

#### SPENT SHALES AS RAW MATERIAL FOR PORTLAND CEMENT

Lastly, it has been suggested that the spent shale could, in part, be used as raw material for the manufacture of portland cement. Mr. R. K. Meade in 1911 reported to the Canadian Government, page 25, Summary Report of Mines Branch of the Department of Mines, for year ending 1911: "These analyses indicate that satisfactory portland cement can be made from a combination of any one of the first three limestones and the residue from the oil-bearing shale," tested by him. Should it be desirable to produce portland cement and should the composition of the spent shale be found suitable for the production of portland cement, with or without the addition of lime to the spent shale, a comparatively small addition to the revolving kiln plant would make that part of this plant suitable for the manufacture, but it is possible, though by no means certain, that the requirements of such manufacture might be found to interfere with the recovery of the nitrogen.

In the plant as indicated there are the possibilities of great flexibility of operation. Such possibilities are entirely absent from the Scotch dual purpose retort, although, because it was a dual purpose retort, flexibility was a most important requisite.



## Recovery of the Nitrogen Contained In Oil Shales

By LOUIS SIMPSON

THE question of the economic retorting of oil-yielding shales will be governed by the results of the retort controversy. Whether the oil shale operators of this continent decide to use the "dual purpose" retort of Scotland, with its elaborate attempt to secure as large a yield of nitrogen as may be possible, or whether they will elect to use a "single purpose" retort, which will give them the largest possible yield of high-grade oil, with a small yield of recovered nitrogen, remains to be seen.

It is a pity that the governments, which are so greatly interested, have not as yet seen their way to aid the operators to solve this question. The proof can be gained only at the risk of a considerable expenditure, much of which would be common to all the tests that would have to be made, hence much duplication of expense would be avoided, were any one or more of the governments interested to arrange for comparative trial runs of the several classes of retorts.

### ECONOMIC COMPARISON OF THE "DUAL PURPOSE" AND "SINGLE PURPOSE" RETORTS

The first question that has to be decided is whether the "dual purpose" retort or the "single purpose" retort is the more economic when operating under the special conditions existing in different parts of the North American continent.

The "dual purpose" retort has been perfected to educe the oil contained in the shale and at the same time to recover to the greatest possible extent the nitrogen contents of the shale. Owing to certain peculiar conditions present in Scotland years ago, this retort was perfected so that the nitrogen contents might be recovered and were recovered even at the expense of the oil contents. The "single purpose" retort is designed so as to make the utmost recovery of the oil contents and so to make such recovery that the risk of cracking the educed oil is lessened. The "double purpose" retort with its necessary accessories is very expensive to build, while the best examples of "single purpose" retorts can be constructed for very much less money. In Scotland, years ago, when the selling price of oil was very low, when gasoline was almost unsalable and when sulphate of ammonia was selling at prices very much higher than pre-war prices, the operators solved the question, so far as they themselves, then, were concerned, by perfecting the "dual purpose" re-

tort. The operations of this retort in Scotland have certainly proved to be very profitable, but it was the local conditions that made the operations of the retort profitable and given other and widely different local and unfavorable conditions, the results would have been very different. The local conditions now existing on the North American continent are nearly, in every item, the opposite to those existing in Scotland when the "dual purpose" retort was perfected, and on this account it is not safe to accept the results obtained in Scotland from the operations of the "dual purpose" retort as the results likely to be obtained by the use of that retort when operated on this continent.

To make this point clear, the conditions that existed in Scotland and the conditions that exist at many, probably at the majority of locations on this continent, are given in Table I, placed side by side for comparison. It is, however, admitted that locations are to be found where the conditions as stated are not present.

The probable future demand for sulphate of ammonia and its market price are quite ob-

TABLE I—COMPARISON OF CONDITIONS IN SCOTLAND AND IN NORTH AMERICA

	As they existed in Scotland	As existing in North America
Shale, quality	Relatively low in oil contents, but high in nitrogen contents	Relatively high in oil contents, but usually low in nitrogen contents
Oil contents	Sale price low	Sale price much higher
Sulphate	Sale price very high	Pre-war sale price very low
Sulphuric acid	Very low in price delivered	Generally high in price delivered
Bagging	Very low in price delivered	Generally high in price delivered
Machinery and repairs	Low in price delivered	High in price delivered
Wages	Low	Before the war double the scale; now probably four times the old rate
Coal	Low in price delivered	Generally dearer, but in this cost great variations will be found
Market for sulphate	World-wide and therefore in constant demand	Local and therefore seasonal, entailing carrying large stocks
Money	Easily obtainable at low interest	Much dearer

secure. It is known that the manufacture of the products of nitrogen has been immensely increased during the war, while the present consumption is probably not larger than it was before the war, if as large. It is known

that much of this increase is from by-product coke ovens, and therefore this source of supply will be persistent in the future, whatever level prices reach. It is known that the remainder of the increase is from processes that obtain the nitrogen from the air, and although it is not certain, it is supposed that these plants will continue to operate.

If sulphate of ammonia and other products of nitrogen are necessary for the welfare of those interested in agriculture, it is not likely that these works, indirectly, in part, paid for by those so interested, will be allowed to lie idle, so that the coke barons and others may charge a high price for a by-product. It is therefore probable that prices will fall to their pre-war level and perhaps lower. Notwithstanding, and in spite of these facts, writers and speakers still persist in claiming that the successful establishment of the oil shale industry depends upon the continued extreme recovery of the nitrogen contained in the shale.

This article is written with the hope of showing that this contention is wrong. Only under special conditions, not often present on this continent, will the utmost possible recovery of the nitrogen in the oil shale become of financial and economic importance and in such rare cases it is possible to add to the approved "single purpose" retort special machinery, especially designed, operated independently from the retort, which will recover the nitrogen as well as if not better than can today be done in the nitrogen recovery section of the "dual purpose" retort.

The axiom still holds good, that by-products should not be manufactured unless the profits accruing upon the money invested in the works and machinery and the working capital necessary for the recovery are equal to or exceed those which would have accrued had the same amount of money been expended in enlarging the output of the original business.

Before a judgment can be arrived at it is necessary that the cost of producing sulphate of ammonia from nitrogen recovered in the "dual purpose" retort be correctly ascertained.

The late Dr. R. W. Ells, in his report published in 1909 by the Canadian Government on the "Oil Shales of New Brunswick and Nova Scotia," has unintentionally been the cause of much misunderstanding on this point.

On page 35 of his report the cost of the "manufacture of sulphate" is given as 46c. per ton shale. It is not stated to what yield of sulphate per ton shale this figure applies, and as the cost in certain items varies with the yield of sulphate per ton shale, the yield becomes a matter of considerable importance. As, however, Dr. Ells on the previous page had mentioned a shale yielding 77 lb. sulphate per ton, it is presumable that the 46c. was given as the cost of manufacturing 77 lb.

of sulphate per ton shale. This cost totals \$11.95 per ton of 2,000 lb. of sulphate.

Authorities in England have given the cost of manufacturing sulphate from ammonia liquor as being before the war as stated in Table II.

TABLE II—COST TO MANUFACTURE SULPHATE FROM AMMONIA LIQUOR		
18 cwt. sulphuric acid at 60 deg. B. at	\$13.33 per ton	\$12.00
3 cwt. lime.....at	\$ 2.40 per ton	0.36
Coke.....		1.10
Bags (containers).....		0.86
Repairs, etc.....		1.10
Labor.....		3.00
Cost in England before the war.....		\$18.42

This cost is considerably higher than that given by Dr. Ells. Dr. Ells gives no details, so it is not possible to explain this wide (50 per cent) difference, which, however, probably consists in the increased cost of acid (the Scotch purchase their acid at a very low cost, delivered), bags and fuel. Perhaps also Dr. Ells forgot to make any allowance for repairs. In neither estimate are included costs of interest, depreciation or management.

Both Dr. Ells' cost and the English cost were costs before the war, and the cost in both countries would have to be considerably increased to represent today's costs, which may safely be taken to exceed \$25 per ton sulphate.

But the \$25 cost represents only the cost of manufacture from ammonia liquor to the sulphate. Besides this cost, the cost of recovering the nitrogen (in the form of ammonia) from the shale must be ascertained.

At this point it may be wise to point out that the objective of the investor of money in the oil shale industry is the winning of dollars upon the dollars invested. It is from this viewpoint that the rival retort processes have to be judged. Therefore to the costs already discussed must be added the extra overhead charges of interest, depreciation and repairs chargeable, owing to the extra cost of the "dual purpose" retort and of its larger exhausters, condensers, pipes and steam boilers, also the extra cost of fuel and water and the extra interest upon working capital required to carry a stock of bags and of sulphate, waiting for shipment to fill the season's orders.

As the making of money is the objective, it is quite legitimate to charge up against the cost of manufacture the interest upon the capital expended, at the rate the money so expended would have earned had it been expended in the recovery of oil from an increased quantity of shale instead of in the recovery of nitrogen and of the manufacture of this nitrogen, so recovered, into sulphate. When this is done, if the total so arrived at is less than the selling price of the sulphate, the



manufacture of this sulphate may be considered, but if the total be more, then, and in that case, the manufacture of the sulphate should be avoided.

To show at a glance how local conditions affect the result, Table III has been compiled. The basis upon which this table has been calculated is as follows:

An installation to treat 1,000 tons of shale per day of 24 hours, 365 days per year. (1) "Dual purpose" retort, plant with sulphate manufacturing costing \$1,200,000. (2) "Single purpose" retort plant without sulphate manufacturing costing \$300,000. Depreciation allowed at 15 per cent per annum, interest calculated at different rates from 50 per cent down to 15 per cent (it is believed that some deposits will make it possible for those operating to earn the larger figures and it is not thought that many will expect to earn less than 15 per cent). The returns of sulphate per ton shale are taken from 70 lb. down to 30 lb. By referring to this table and by adding the figure found, where the interest and the per cent of sulphate meet, to the \$25 before mentioned, a total will be reached that will indicate nearly the actual cost of the sulphate, when made by the use of the "dual purpose" retort.

It is believed that the \$25 cost per ton for manufacture, which has to be added to the above, is far too low a present estimate; but

TABLE III—COST OF SULPHATE  
(Overhead and Profit only)

	70 lb. per ton shale	60 lb. per ton shale	50 lb. per ton shale	40 lb. per ton shale	30 lb. per ton shale
50%	\$45.79	\$53.42	\$64.10	\$80.13	\$106.84
40%	38.73	45.20	54.24	67.80	90.40
30%	31.70	36.98	44.37	55.47	73.96
25%	28.17	32.87	39.44	49.30	65.74
20%	24.65	28.76	34.51	43.14	57.52
15%	21.13	24.66	29.59	36.99	49.32

using that cost as a basis, the following results are obtained:

Where oil discovery alone would yield only 15 per cent profit on the capital employed and with shale yielding 30 lb. sulphate per ton the cost would be \$74.32 per ton; where the

oil yields 50 per cent profit, the cost of sulphate would be \$131.84 per ton. With 50 lb. shale the low cost would be \$54.59 and the high cost \$89.10. Seventy lb. sulphate per ton shale is an exceptional return. But to the above total a further charge may have to be added in cases where the capital at command is not sufficient to warrant the erection of a 1000-ton plant using the "dual purpose" retort. In many cases where only 250 tons per day are mined and assembled instead of 1000 tons, it may be assumed that the cost of mining, assembling, and of management will be increased by 25c. per ton of shale. This 25c. per ton shale when retorting shale that yields 30 lb. sulphate of ammonia increases the cost per ton sulphate by no less than \$15.

Mention has been made of a possible arrangement by which the nitrogen left in the spent shale can be conveniently recovered. There is no doubt that were the spent shale from a 1000-ton shale unit treated in a revolving horizontal kiln (especially in such cases where the shale contains considerable fixed carbon), it would be possible to recover not only a very high percentage of the nitrogen, but also, if found desirable, the potash contents.

#### CONCLUSIONS

1. The "dual purpose" retort is only of interest when exceptional conditions are present, conditions that are not often met with on the North American continent.

2. The future of the oil shale industry is largely dependent upon the construction of a "single purpose" retort that can be erected at a low cost and which will recover the maximum quantity of oil.

3. It is possible to arrange for a machine which operates independently from the "single purpose" retort, which will recover the contents of nitrogen even more completely than can be done in the nitrogen recovery end of a "dual purpose" retort.

4. Some nitrogen, if desired, can be recovered from the "single purpose" retort, but such recovery is not advisable unless sulphuric acid is obtainable at a low price delivered or unless there be a good local market for the sulphate.

## Pressure and Temperature Relations for Vapor of Liquids

BY P. B. WILLIAMSON

RECENTLY while working out the design of a cracking process for producing gasoline, it was necessary to have, among several other things, some quantitative idea of the change under different pressures of the boiling points of quite a large number of hydro-carbons—especially of the paraffines. On consulting a number of authorities it was found that very little had been published on the vapor-tension phenomena of those compounds and furthermore that substantially nothing had been done toward determining a general expression involving the pressure on a liquid and the latter's boiling point under that pressure—or, in physicochemical terms, the general relation between the temperature of a liquid and its corresponding vapor tension. A search for information on the subject, including, as it did, correspondence with some of the leading physical chemists and research institutions of America, forcibly brought to mind a statement written by the author several years ago in his physics lecture notes: "No definite law is known (1910) connecting the boiling point of a liquid with the pressure; all we can say in general is that the greater the pressure, the higher the boiling point." It is apparent, however, that if such a law does exist, its application would be extremely valuable: First as a check on experimental work on the vapor-tension variation of liquids; secondly, as a check on the normal boiling point, melting point and density of liquids; and thirdly, for practical determination of the vapor-tension behavior of liquids on which no vapor-tension data have yet been published.

### BERTRAND'S EMPIRICAL FORMULA

In reviewing the literature it was found that Bertrand had investigated twenty-two liquids and found the following equation to be applicable to them:

$$P = G \left( \frac{T_p - \lambda}{T_p} \right)^g \quad (1)$$

where

$g = 50$  for twenty-one of the compounds and 20 for chloroform.

$P =$  pressure in mm. of mercury.

$T_p = 274 +$  pressure boiling point in deg. C.

$G, \lambda =$  constants peculiar to each liquid.

The use of this formula entails the determination for each liquid of three constants,

$g, G$  and  $\lambda$ . In order to simplify the expression the first step made was to modify (1) so as to give the pressure in atmospheres, to do which the following analysis rapidly ensued:

$$P \div p = \text{a constant, } c \quad (2)$$

where  $p =$  pressure in atmospheres, 760 mm.

Then from (1) for  $p_n =$  normal pressure, 1 atmosphere

$$c = P_n = G \left( \frac{T_b - \lambda}{T_b} \right)^g \quad (3)$$

where  $T_b =$  normal b.p. (abs.) of the liquid.

Substituting (3) in (2) and then multiplying by  $p$  gives

$$P = pG \left( \frac{T_b - \lambda}{T_b} \right)^g \quad (4)$$

Whence, from equating the identities (1) and (4) and solving for  $T_p$ , we get

$$T_p = \frac{\lambda}{1 - \frac{T_b - \lambda}{T_b} \sqrt[g]{p}} \quad (5)$$

from which the constant  $G$  has thus been eliminated.

Bertrand reckoned from an absolute zero of  $-274$  deg. and obtained the values of  $\lambda$  enumerated in the table given in sec. 5, p. 520, vol. 1, of Gastell-Evans' "Physico-Chemical Tables" (Griffin, London, 1902-11). For an absolute zero of  $-273.1$  deg. those values must be modified accordingly.

### VAPOR TENSION CONSTANT EXPRESSIONS

Having derived equation (5) it was decided to determine whether there exists a definite relation for each compound between its "vapor-tension constant,"  $\lambda$ , and certain of its properties, such as melting points, boiling points, densities and molecular weights.

It is hardly necessary to state that considerable disagreement arises in several instances as to the value assigned to the various properties, such as, for example, the melting point of  $\text{CO}_2$ , the boiling point of  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ , etc., and on various densities. Naturally the densities must be reduced to some standard; which was taken as 273.1 deg. abs.

Omitting quite a lot of detail, it would appear that  $\lambda$  is given by an equation, say, of the form

$$\lambda = \alpha T_b^\beta T_m^\gamma d^\delta (\log W)^\eta \quad (6)$$

in which the coefficient  $\alpha$  and the exponents  $\beta, \gamma, \delta$  and  $\eta$  are probably universal constants.



The most probable values of these constants may be found from a large number of liquids (using the most positive values of their properties) by solving by the method of least squares the following equation:

$$\log \lambda = \log a + \beta \log T_b + \gamma \log T_m + \delta \log d + \eta \log \log W \quad (7)$$

Not having good facilities for the immense amount of calculation the above method involves, nor the opportunity of determining the correct data needed therefor, no attempt has been made to derive the above constants precisely. It will be shown, however, that a general formula for  $\lambda$  can be found involving only the comparatively well-known constants of the specified liquid—if not of the form just suggested, yet of some other type of algebraic expression.

According to Bertrand, in his equation (1), for chloroform  $g = 20$  and  $\lambda = 120$ . But using equation (5), for chloroform  $g = 50$ , as with the other liquids investigated by Bertrand, and  $\lambda = 61.6$ , which agrees with (6) within the limits of error of the data used. Furthermore, approximate calculations on a large number of compounds picked out at random from the vapor-tension tables in Castell-Evans, pp. 451-523 (vol. 1), considering the limits of error established by the agreement of the authorities quoted therein, make it appear that Bertrand's constant  $g = 50$  is probably universal.

The constant  $\lambda$  may be experimentally determined for liquids having no published vapor-tension tables. Thus, rearranging (5) and putting  $g = 50$ , we get

$$\lambda = \frac{T_p T_b (\sqrt[50]{p} - 1)}{T_p \sqrt[50]{p} - T_b} \quad (8)$$

When the pressure is normal ( $p = 1$  atmosphere), then  $T_p = T_b$ , and those values substituted in (8) give  $\lambda = 0 \div 0$  (indeterminate). Neither by rearrangement nor by successive differentiation of the numerator and denominator of the right-hand side of (8) can the indeterminate form be got rid of. That fact can be proved mathematically, but the proof is too long for inclusion here; and, anyhow, it is apparent that any reduction of (8) to normal pressure will give the constant  $\lambda$  in terms of the normal boiling point  $T_b$ . That  $\lambda$  does not depend upon  $T_b$  alone readily shows from even a casual inspection of the table. However, by finding a number of boiling points for different pressures (other than normal) a mean value of  $\lambda$  follows from (8).

#### DEGREE OF PRECISION OF APPLICATION OF $\lambda$

Remarking further on positiveness of tables: Probably the most reliable vapor-tension table given in Castell-Evans is that for water, on p. 461 (vol. 1). Substituting pairs of correspond-

ing values from that table in equation (8) shows that the different values of  $\lambda$  thus obtained do not coincide. Thus, for example,

$p$	$T_p$	$\lambda$
10	453.41	78.41
50	537.67	78.35
1.70	625.1	78.94

Since the values of  $\lambda$  thus calculated do not vary uniformly with the pressure  $p$  (as they should do, were there any theoretical variation), but rather, "oscillate," it follows that the thermometry of the table is not exact. In the same manner and, it is reasonable to suppose, on the same account the values of  $\lambda$  calculated from the tables for other liquids vary according to the positiveness of the thermometry involved.

Bertrand's value for water of  $\lambda$ , referring to absolute zero as  $-274$  deg., is 78.3. That value referred to an absolute zero of  $-273.1$  deg. becomes 78.112. By striking a mean among the values calculated back from the table for water by (8), we get  $\lambda = 78.5$ . The same order of difference applies to  $\lambda$  for those of the other liquids checked. It would appear, then, that Bertrand's values need revision. For engineering calculations, however, all of the variations mentioned so far may be overlooked.

In conclusion, referring to equation (19) it follows the following relation should hold:

$$\lambda = 0.0081WL_b \quad (19a)$$

More or less empirical methods have been tried above, deriving expressions involving a constant to be found for each liquid either by experiment or by possibly evolving a general equation for the constant itself. As the first determination, for authoritative purposes, would require considerable laboratory work and the second determination might entail no less and probably much more labor for the theoretical chemist, it seemed desirable to approach the subject from another angle, with the rather astonishing results below.

#### DIFFERENTIAL RELATIONS

Consider the unsaturated vapor of a pure liquid: From the standpoint of differential relations, it seemed possible that a general solution might ensue from the familiar linear equation always coming up when dealing with "single-energy" effects, viz.:

$$\frac{dT}{dp} + X_1 T = X_2 \quad (9)$$

where  $X_1$  and  $X_2$  may or may not involve  $p$ .

The standard solution of (9) is

$$T = e^{-\int X_1 dp} \cdot (f X_2 e^{\int X_1 dp} \cdot dp + C) \quad (10)$$

where  $e$  is the Napierian base and  $C$  is an integration constant dependent upon the terminal conditions of the problem.

From the nature of the problem the standard solution (10) calls for any of three combinations, viz.;  $X_1$  and  $X_2$  both involve  $p$ ;  $X_1$  is a constant and  $X_2$  involves  $p$ , and  $X_1$  involves  $p$  and  $X_2$  is a constant. The simplest choice is the last. Now the curve plotted between absolute temperatures as ordinates and corresponding pressures as abscissæ theoret-

trioxide to  $\tau = 2.17$  for liquid helium, with an average around 0.8.

#### SOLUTION OF THE VAPOR TENSION CONSTANT $\tau$

The difficult with indeterminate forms is met with upon attempting to evaluate  $\tau$  from (12). But, taking another tack (cf., e.g., "The Principles of Physical Chemistry," by E. W. Washburn, 1st ed., 1915, McGraw-Hill, N. Y., Chap XII, esp. secs. 1, 2, etc.) this obstacle may be avoided by the use of the well-known expression

$$\left(\frac{\delta p}{\delta T}\right)_{p_1 x} = \frac{L_v}{v_0 T} \quad (13)$$

where

$L_v$  = molal heat of vaporization of the liquid

$v_0$  = molal volume of the liquid in the vapor state under conditions  $p_1, x$ .

For a theoretically perfect vapor (13) is integrated by

$$\ln \frac{p_1}{p_2} = \frac{L_v}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (14)$$

in which

$\ln$  = natural logarithm

$R$  = the universal gas constant dependent only upon the units employed.

Now if we put  $p_1 = p$ ,  $p_2 = 1$  atmosphere,  $T_2 = T_b$ , and  $T_1 = T_p$  in (14), then

$$\ln p = \frac{L_v}{R} \left( \frac{1}{T_b} - \frac{1}{T_p} \right) \quad (15)$$

But  $L_v$  varies with the temperature in the same manner but in different degree for each liquid and, therefore, introduces the necessity for its positive determination accordingly—as a general rule quite a task within itself. But by considering differential increments  $\Delta p$  and  $\Delta T$  as added, respectively, to the normal pressure and boiling point, it may be written

$$\left. \begin{aligned} p &= 1 + \Delta p = p \\ T_p &= T_b + \Delta T = T \\ L_v &= L_{vb} \end{aligned} \right\} \quad (16)$$

$$\text{But } L_{vb} = WL_b \quad (17)$$

where

$L_b$  = latent heat vaporization (say, in calories per gram) at the normal boiling point of the liquid.

$W$  = molecular weight of the liquid.

The last assumptions, then, transform (15) into

$$\ln p\delta = \frac{WL_b}{R} \left( \frac{1}{T_b} - \frac{1}{T_\delta} \right) \quad (18)$$

$$T_\delta = 1 \div \left( \frac{1}{T_b} - \frac{R}{WL_b} \cdot \ln p\delta \right) \quad (19)$$

Now from (12)

BERTRAND'S A TABLE

Substance	Formula	$\lambda$	$T_m$	$T_b$	$W$	$\log W$	$d$
Carbon dioxide	CO <sub>2</sub>	35	195	217	44	1.6435	1
Hydrogen sulphide	H <sub>2</sub> S	37.1	188	212	34.1	1.5326	0.88
Ammonia	NH <sub>3</sub>	46.7	195	235	17	1.2313	0.623
Cyanogen	(CN) <sub>2</sub>	47.3	239	252	26	1.4151	0.88
Boron trichloride	BCl <sub>3</sub>	48.8	291	117.4	2	0.696	1.434
Sulphur dioxide	SO <sub>2</sub>	49.5	197	263	64.1	1.8067	1.434
Ethyl chloride	C <sub>2</sub> H <sub>5</sub> Cl	50.5	132	293	64.5	1.8096	0.921
Cyanogen chloride	(CN)Cl	53.1	255	269	61.5	1.7887	1
Carbon disulphide	CS <sub>2</sub>	54.8	163	319	76.1	1.8816	1.292
Ethyl bromide	C <sub>2</sub> H <sub>5</sub> Br	55	157	312	109	2.0373	1.45
Ethyl ether	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	55.4	156	308	74.1	1.87	0.73
Silicon tetrachloride	SiCl <sub>4</sub>	57.9	184	332	170.1	2.2308	1.524
Ethyl iodide	CH <sub>3</sub> CH <sub>2</sub> I	60.6	165	345	156	2.193	1.96
Phosphorus trichloride	PCl <sub>3</sub>	61.6	161	349	137.4	2.1381	1.613
Chloroform	CHCl <sub>3</sub>	61.6	210	335	119.4	2.077	1.526
Carbon tetrachloride	CCl <sub>4</sub>	61.7	248	350	153.8	2.1871	1.6
Methyl alcohol	CH <sub>3</sub> OH	71.5	179	340	32	1.5056	0.81
Ethylene bromide	CH <sub>2</sub> Br·CH <sub>2</sub> Br	72.9	283	405	187.9	2.2739	2.1
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	76	161	351	46.1	1.6635	0.81
Pinene	C <sub>10</sub> H <sub>16</sub>	76.8	429	136	1	2.134	0.89
Water	H <sub>2</sub> O	78.3	273	373	18	1.2557	1
Acetic acid	CH <sub>3</sub> COOH	78.6	290	391	60	1.7784	1.03
Sulphur	S	135	390	717	32.1	1.5061	2
	S <sub>2</sub>				64.1	1.8071	

ically is parallel to the axis of abscissæ when the pressure is infinite; i.e., when  $p = \infty$  then  $dT \div dp = 0$  and  $X_1 T = X_2$ . But if  $X_1$  involves  $p$  in a certain way then  $0 = X_2$  when  $p = \infty$ , or by the third assumption  $X_2$  is constantly zero; which reduces (10) to

$$T = Ce^{-ff(p) \cdot dp} \quad (11)$$

Since the temperature of the liquid has only a theoretical value when the vapor pressure of the liquid is zero, consideration of the terminal conditions as those when  $p$  is zero takes us rather too much into the abstract. It is more convenient to consider the integration-constant reference conditions as those under the normal pressure of one atmosphere; thus obtaining from<sup>1</sup>

$$T_p = T_b e^{\tau(p\zeta - 1)} \quad (12)$$

where

$T_p$  = temperature of the liquid (absolute C.)

$T_b$  = normal boiling point (abs.) of the liquid

$T_p$  = vapor tension of the liquid in atmosphere

$\tau, \zeta$  = constants peculiar to each liquid.

Upon applying (12) to over 125 liquids for which the writer had to hand vapor-tension

tables, it was found that while  $\zeta = \frac{1}{9}$  (approx.)<sup>1</sup> for all of those liquids, on the other hand,  $\tau$  varied from  $\tau = 0.567$  for arsenic

<sup>1</sup>Thus corresponding to the linear equation  $\frac{dT}{dp} - \frac{\tau}{9} p^{-\frac{8}{9}} T = 0$



$$\tau = \frac{\ln(T_p \div T_b)}{p^\zeta - 1} \quad (20)$$

Substituting (19) in (20) gives

$$\tau = \frac{-1}{p^\zeta - 1} \cdot \ln \left( 1 - \frac{RT_b}{WL_b} \cdot \ln p^\delta \right) \quad (21)$$

The smaller the value assigned to  $\Delta p$ , the more accurate is the relation (21) and, at the same time, the closer to an infinitesimal<sup>2</sup> is  $\ln p^\delta$ . Hence, taking advantage of the expansion

$$\ln(1 - x) = -x - \frac{1}{2}x^2 - \frac{1}{3}x^3 - \frac{1}{4}x^4 - \dots \quad (22)$$

the terms beyond the first on the right-hand side may be disregarded and thus enable us to reduce (21) to

$$\tau = R_1 \frac{T_b}{WL_b} \quad (23)$$

where  $R_1$  involves  $R$  and  $\zeta$ , which are practically the same for all the liquids investigated. Checking (23) against water, mercury, ether, etc. (in fact, against over fifty liquids, and solids and gases in the liquid state), gives the almost exactly general value  $R_1 = 17.42$  (slide rule); that is,

$$\tau = 17.42 \frac{T_b}{WL_b} \quad (24)$$

an expression involving only the comparatively better known constants of a liquid—the normal boiling point, the molecular weight, and the latent heat of vaporization (at normal b.p.) of the liquid.

#### A GENERAL VAPOR TENSION TEMPERATURE LAW

The foregoing analysis gives a basis for the statement that: The temperature of a liquid varies with changing vapor tension according to the logarithmic law; the natural logarithm of any particular temperature (absolute) being equal to a known function of the vapor pressure, plus the natural logarithm of the normal boiling point, or, algebraically

$$T_p = \text{iln} \left[ 17.42 \frac{T_p}{WL_b} (\sqrt[p]{p} - 1) + \ln T_b \right] \quad (25)$$

or, using common logarithms,

$$T_p = \text{ilog} \left[ 7.56 \frac{T_p}{WL_b} (\sqrt[p]{p} - 1 + \log T_b) \right] \quad (26)$$

By rearranging (26) an expression for vapor pressure (atmos.) is obtained (27)

$$p = \left[ 1 + 0.1325 \frac{WL_b}{T_b} (\log T_b - \log T_p) \right]^9 \quad (27)$$

and for latent heat (calories per gram at normal b.p.) in (28)

$$L_b = 0.1325 \frac{W}{T_b} (\log T_p - \log T_b) (\sqrt[p]{p} - 1)^{-1} \quad (28)$$

Since the pressure on a liquid is equal in magnitude to the vapor tension (pressure) of the liquid when boiling under that pressure, equation (26)—or (25), or (12) with (24)—arrives at an answer to the question often asked in practice:

"What will be the boiling point of so-and-so when the pressure on it is increased or decreased to such-and-such a value above or below normal?"

Cracking-process engineers, among others, will quickly recognize the query. In applying (26) to petroleum, however, Dalton's Law of Partial Pressures must be considered. In fact, the application to any mixture, whether a constant-boiling one or a fractional-distillation one, supplies enough material for another paper on the subject.

Equation (27), inversely, arrives at conclusions regarding pressures—coming up, say, in superheating problems, etc.

Equation (28) might lead to another method for checking the latent heat of vaporization at the normal boiling point. By experimenting upon a substance whose latent heat determination presents especial difficulty by former methods, a table of temperatures and corresponding pressures may be developed (for the sake of obtaining a mean), and therefrom the value of  $L_b$  computed by (20).

Going further, if a substance should present itself and its latent heat and a table similar to that just mentioned can be found, then the molecular weight of the substance directly follows from (28) as

$$W = 7.56 T_b L_b (\sqrt[p]{p} - 1) (\log T_p - \log T_b)^{-1} \quad (29)$$

From Berthelot's equation (cf. Washburn, *loc. cit.*, Chap. II, p. 36, etc.)

$$W = DRT_b \left[ 1 + \frac{9T_c(T_b^2) - (6T_c^2)}{128p_c T_b^3} \right] \quad (30)$$

where

$D$  = density of vapor at normal b.p.  
 $T_c$  = critical temperature (abs.)  
 $p_c$  = critical pressure (in atmospheres)  
 $R$  = the gas constant (dependent upon density unit employed).

From (30) there may be obtained an equation for  $T_c$ , the critical temperature, or for  $p_c$ , the critical pressure, which in connection with (26) or (27) gives a check on either of those properties of a substance. The equations are

<sup>2</sup>Of a higher order than  $p^\zeta - 1$ .

rather involved—yet worse things could be encountered. It is hardly necessary to state that any property sought in one of the above ways should depend only upon data from other sources, and not upon values previously found by (26) or its modifications.

Appended herewith is a table showing, within the limits of error or of agreement of the data consulted, the remarkably close toeing-to-the-mark of enough substances to justify the above theoretical conclusions. For quite a number of substances no latent-heat figures could be found in references at hand; in which cases, for the purpose of comparison, the latent heat was computed by Trouton's Rule, viz.:

$$\frac{WL_b}{T_b} = \eta \text{ (a constant)} \quad (31)$$

where  $\eta$  is the same for similar liquids. Referring (31) to (24) shows that

$$\tau = 17.42 \div \eta \quad (32)$$

#### APPLICATION OF THE RELATIONSHIPS

Discussing the general results of the application of the formulæ, it must be said at the outset that they checked much better than had been anticipated. Only three really glaring departures occur—those of formic acid, acetic acid, and acetic anhydride. But it is to be noted that  $\tau$  approaches 0.75 from the tables for those three; which is following Trouton's assumption. Also, according to Trouton's Rule, if the latent heats of the three variants are correct as given, then the acetates and the formates should also prove exceptional; but those last, as seen, are among the best performers. Only one latent-heat reference each for formic acid and acetic anhydride could be found; but no less than three widely different values (all at the b.p., of course) were in evidence for acetic acid. Until something more definite regarding the latent heats of those discrepant liquids is forthcoming, the writer feels justified in believing that some peculiar difficulty is attached to the determination of that property of theirs.

The latent-heat data on sulphur were also hopeless (as is usual with  $S_2$ ), and that particular instance was dismissed with the "stroke" of using for  $S_2$  the Trouton Number ( $\eta$ ) of  $O_2$ .

The propionates, butyrates and valerates appear a little irregular, but a reasonable doubt may be cast upon the thermometry of the tables consulted for them, as well as upon the latent heats given.

In numerous instances of iso-compounds  $\tau$  is checked better by the formula if the latent heat of the corresponding normal compound be substituted therein.

Only in two or three instances did there seem to appear any tendency to stray away

from the value  $\frac{1}{3}$  for  $\zeta$  (in which cases the thermometry was clearly equivocal). The value of  $\zeta$  begins to change, however, near the melting point. For example,  $\zeta = \frac{1}{3}$  for water from 50 deg. (cf. K. & L., p. 40) to the critical temperature. Below 50 deg.  $\zeta$  changes. That was to be expected from the fact that the present analysis assumes an unsaturated vapor.

Some of the rather pleasing results obtained are the apparent agreement of the gases of extremely low boiling point, of niton (radium emanation), and the figures for arsenic trioxide. The last is a subliming substance, and no boiling point has been found for it heretofore. A theoretical boiling point was, therefore, deduced for  $As_2O_3$  by determining  $\tau$  from simultaneous equations, thus:

$$\tau = \frac{\ln T_p - \ln T'_p}{\frac{1}{p} - \frac{1}{p'}} \quad (33)$$

Then, having  $\tau$ , the theoretical value of  $T_b$  is obtainable from (12); proving to be 650.1 deg. abs. or 377 deg. C. Using that value gives the proper agreement, and the check for  $\tau$  (against  $AsCl_3$  is very close, considering. But what to do with carbon dioxide is a question.

The desirability of using the most positive data obtainable should be emphasized, or in the case of having several authorities, of striking a most probable mean (if necessary, drawing an average curve), it being also advisable, when a lone table is in doubt, to plot a curve which will show whether or not the tabulated data give all points on or very nearly on a smooth curve: e.g., plot a curve between  $x = \text{mm.}$  and  $y = t$  from the table cited for m-amidoxylene. In the heading (p. 42) to their vapor-tension tables Kaye and Laby advise caution: "The thermometry is in many cases somewhat dubious."

Some of the earlier investigators performed monumental labors in producing tables and in working out interpolation formulæ; yet more modern workers, notably Ramsay and Young, with advantage of more refined methods and apparatus and using stricter criteria, have obtained results that in quite a number of instances, especially at extreme pressures and temperatures, differ very appreciably from those of their predecessors. But it is wonderful, indeed, how much, aside from laying foundations, those searchers of the middle nineteenth century accomplished!

No attempt, therefore, has been made to give long-drawn-out accuracy either to the numerical values in the foregoing equations or to the figures on the table, owing, as just explained, to certain doubts about single-source data and to the disagreement, sometimes close,



sometimes wide, of the authorities consulted for multiple-source data. The main thing is a desire to point out that here is a case where in all liquids—whether mercury, sulphur, cadmium, xenon, water, ether, alcohol, normal compounds, iso-compounds, or what not—ap-

parently follow the same law; which, naturally, leads one to believe that similar general laws exist for other property variations (or for the properties themselves)—such as, for example, variation with temperature of latent heat of vaporization, of viscosity, etc.

## Calculations with the Williamson Formula

BY WALLACE SAVAGE

Some months ago Mr. Williamson contributed his modification of Bertrand's empirical vapor pressure formula in editorial correspondence. Publication of it was withheld until the present time because it did not seem to offer sufficient aid to the overburdened-with-computations engineering profession. However, a new formula, as subsequently developed, can readily be worked with by means of a ln-log slide rule or an alignment chart having similar scales together with a special ninth root scale. Such a chart was designed by the writer and is included herewith.

Upon inspection of it, the reader will observe first the three equidistant scale lines  $X$ ,  $Y$  and  $Z$ .  $Z$  and  $X$  are simple 6-in. log scales and  $Y$  has a log scale unit one-half as long, the initial points of the units being in line (1.00, 100 and 100). It is mathematically evident<sup>1</sup> that any straight line connecting an  $X$  number with a  $Z$  number will give the product of the  $XZ$  numbers on  $Y$ . Thus, 150 connected with 2 intercepts 300 on  $Y$ .

In the formula  $\tau(P^{\frac{1}{3}} - 1) = \ln T/T_B$ , the values of  $\tau$ , being simple, are assigned directly to the  $Z$  scale. Values of the expression  $(P)^{\frac{1}{3}} - 1$  are then computed and scaled at any convenient intervals above  $X$  on the three lines 1, (Values of  $P$  1.002 — 1.02 and 0.998 — 0.998 atmospheres); 2, (1.2 — 2.0 and 0.98 — 0.50) and 3, (1.2 — 100 and 0.83 — 0.005). Thus on the third line, 2 atm. and its reciprocal 0.5 are placed at  $(2^{\frac{1}{3}} - 1)$  or  $(1.08 - 1) = 0.080$ , or 80 as expressed in the  $X$  scale units.  $\ln T/T_B$  are then scaled in a similar manner over  $Y$  on the three lines 1, 2 and 3 so as to be equidistant from  $Z$  and the corresponding  $P$  lines. Thus four separate alignment charts are obtained in a stack having the  $Z$  scale in common.

Upon making many calculations on liquids having known vapor pressures, it was found that the formula was very accurate at temperatures above the boiling point. Very large relative errors were found at lower temperatures, making it seem necessary to vary  $\tau$  or  $\tau$  of the original formula. The latter

seemed the more logical because  $\tau$  is inversely proportional to  $W$ , the molecular weight of the liquid, which increases with polymerization, and  $L_B$ , the latent heat of evaporation, which also increases. The following data on water and benzol may be taken as typical:

WATER $T/T_B = T/373$									
Deg. C...	370	250	200	150	70	40	20	0	
$T/T_B$ .....	1.72	1.40	1.27	1.13	0.92	0.84	.785	.732	
Press. Atm.	207	39.1	15.3	4.85	.307	.073	.023	.006	
Cal. Tau..	0.67	0.67	0.67	0.67	0.67	0.52	0.47	0.43	

BENZOL $T/T_B = T/353.4$									
$T/T_B$ .....	1.49	1.35	1.20	.976	0.89	.833	.776		
Press. Atm....	29.3	14.0	5.70	0.72	.238	.098	.035		
Cal. Tau.....	0.89	0.89	0.89	0.65	0.67	0.63	0.57		

Thus readings for water on the chart are correct with  $\tau$  at 0.67 on  $Z$  for all points connecting it with the  $T$  (1) —  $P$  (1),  $T$  (2) —  $P$  (2) and  $T$  (3) —  $P$  (3) scales excepting from 0.30 to 0.005 on the lower side of  $P$  (3). However, if a point opposite 0.71 and one-third distant to the  $T$  (3) scale is taken, it will be found to determine these lower temperature ratios and pressure readings to a fair degree of accuracy.

The reader is cautioned not to get his scales mixed, bearing in mind that he has four separate and distinct alignment charts, the  $T$  and  $P$  scales of which have reciprocals, which are always to be used together. The  $X$ ,  $Y$  and  $Z$  chart is given for use in the simple multiplications and divisions required in calculating millimeters, absolute boiling fraction temperatures, etc.

The table of constants included here has two  $\tau$  values, the first as determined empirically from known vapor pressures and the second from the substitution of  $L_B$  in the formula for  $\tau$ . Where molecular dissociation occurs, the values of  $\tau$  tend to increase greatly. To make the formula and chart 100 per cent reliable, it will be necessary to have empirical  $\tau$  values throughout the entire range of temperature to be considered.

<sup>1</sup>For a geometrical proof and discussion, see Lipka, Graphical and Mechanical Computations, p. 45.

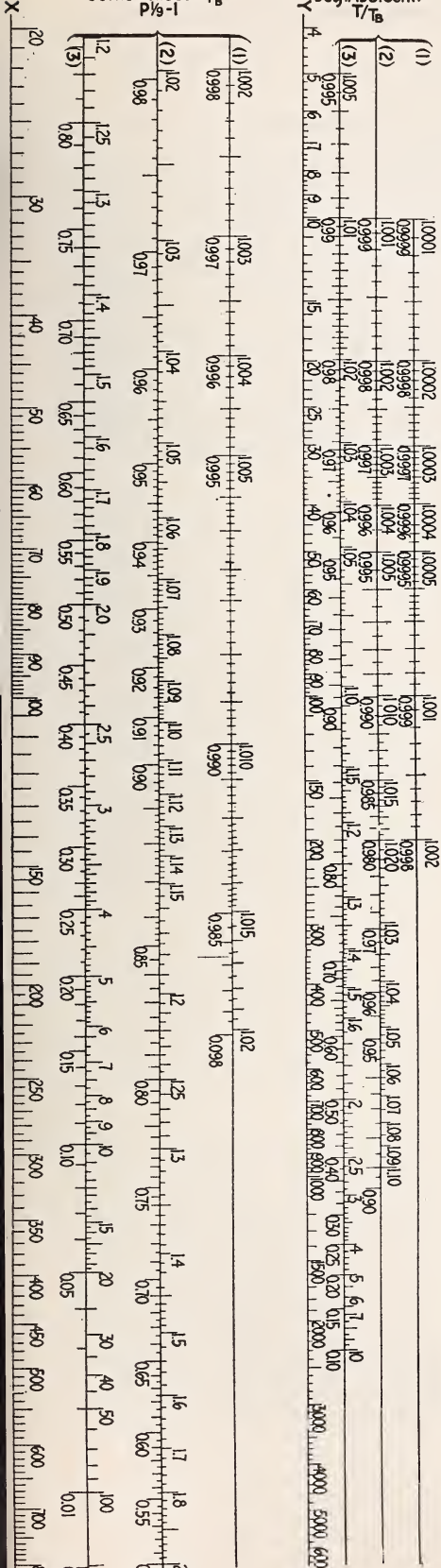
WILLIAMSON FORMULA CONSTANTS AND AN ALIGNMENT CHART FOR GRAPHICAL COMPUTATION

$T_B$	$\tau$	$T_L$	$L_B$	$\tau$	$T_L$	$L_B$	$T_B$	$\tau$	$T_L$	$L_B$
Hydrogen.....	3.0	1.4	123	0.57	0.76	650	Chlorobenzene.....	405	0.84	72.5
Sodium.....	1.50	1.4	592	0.76	0.85	429	Bromobenzene.....	429	0.84	56.5
Potassium.....	1.030	0.78	403	0.85	0.85	354	Bromonaphthalene.....	354	0.84	58.6
Magnesium.....	2.470	.....	.....	0.85	0.85	405	Ethyl bromide.....	405	0.85	43.8
Aluminum.....	2.470	.....	.....	0.85	0.85	51	Ethylene bromide.....	447	0.76	.....
Lead.....	2.540	0.7	430	0.85	0.85	30	Ethyl iodide.....	345	0.82	47.2
Tin.....	1,800	0.80	529	0.85	0.85	.....	Iodobenzene.....	462	0.82	48.2
Bismuth.....	1,690	0.60	592	0.85	0.85	.....	Fluorobenzene.....	358	0.85	47.7
Arsenic.....	234	0.60	656	0.85	0.85	.....	Cyanogen chloride.....	252	0.79	77
Phosphorus.....	980	0.55	108	0.9	0.88	134	Acetylene.....	330	0.84	11.5
Nitrogen.....	79	0.96	188	0.9	0.88	124	Ethyl ether.....	125	0.79	87.5
Oxygen.....	90	0.85	58	0.85	0.88	75	Carbon disulphide.....	300	0.84	87.5
Sulphur.....	232	0.84	228	0.88	0.96	85	Ethyl acetate.....	374	0.84	76.5
Chlorine.....	239	0.88	342	0.85	0.88	85	Propyl acetate.....	393	0.84	71.5
Bromine.....	332	0.80	371	0.85	0.87	74	Ethyl butyrate.....	353.4	0.81	82.5
Iodine.....	438	0.79	398	0.82	0.87	.....	Toluene.....	354	0.81	79
Manganese.....	2,470	.....	446	0.76	0.83	153	Acetylene.....	412.9	0.8	78.3
Iron.....	2,720	.....	170	0.76	0.68	266	Diethylene.....	410.5	0.8	78.3
Copper.....	1,180	0.65	338	0.68	0.64	206	Nitrobenzene.....	481	0.751	90.5
Zinc.....	2,220	0.71	351	0.64	0.65	164	o-nitrotoluene.....	493	0.751	83.3
Silver.....	1,040	0.90	370	0.66	0.65	137	m-nitrotoluene.....	512	0.751	84.5
Cadmium.....	2,800	0.80	381	0.66	0.66	120	p-nitrotoluene.....	517	0.751	86.4
Gold.....	373	0.67	403	0.66	0.66	56	Aniline.....	437	0.751	113.9
Mercury.....	321	0.85	249	0.84	0.88	46	m-nitroxybenzene.....	472	0.77	102.7
Hydrogen sulphide.....	211	0.86	354	0.85	0.84	55	p-toluidine.....	476	0.751	103.1
Hydrochloric acid.....	190	0.77	382	0.84	0.84	92	p-chloroxybenzene.....	491	0.751	94
Hydrobromic acid.....	204	0.87	341	0.72	0.77	57	Phenol.....	491	0.70	.....
Nitric acid.....	228	0.84	420	0.82	0.82	44	m-anisidoxylene.....	456	0.75	.....
Ammonia.....	240	0.85	435	0.77	0.77	.....	Naphthalene.....	624	0.75	.....
Nitrous oxide.....	180	0.66	458	0.82	0.82	.....	Anthracene.....	624	0.75	.....
Nitric oxide.....	123	0.66	.....	0.77	0.77	.....	.....	.....	.....	.....
Nitrogen pentoxide.....	295	0.80	.....	.....	.....	.....	.....	.....	.....	.....



Vapor Pressure - Temperature Alignment Chart  
Based on Formula  $\log \frac{P}{P_0} = \frac{L_B}{T - T_0}$

$T_0$  = Boiling Point Abs. C. Deg.  
 $L_B$  = Latent Heat Evaporation  
 $W$  = Molecular Weight  
 $P$  = Pressure in Atmospheres  
 $e$  = 2.718, Natural Log. Base





## PROBLEM SOLUTIONS

What is the vapor pressure of mercury at 450 deg. C.? The absolute temperature is first found by adding 273, giving 723 deg. for  $T_p$ . Upon looking through the constants of the elements in the first column, the absolute boiling point of mercury is found to be 630 deg. and tau 0.80. The ratio of  $T_n$  to  $T_B$  is then found to be 1.15 by aligning 630 on  $X$  with 723 on  $Y$  and taking the point of intersection on  $Z$  of this line. The pressure is then found by aligning 0.80, the value of tau, on  $Z$  with 1.15 on  $T(3)$ , the point of intersection on  $P(3)$  giving the pressure as 4.4 atmospheres. This is readily converted to millimeters of mercury by aligning 760 on  $X$  with 4.4 on  $Z$ , giving a line that intersects  $Y$  at 3340. Upon looking up the determined mercury vapor pressures in Landolt and Börnstein Tabellen, page 376, five values are given as follows:

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Regnault.....	450 deg. C.	3384.4 mm.
Hertz.....		3229
Ramsay & Young.....		2996.1
Jewett.....		3245.0
Young.....		3 50.5

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If it had been desired to know to what temperature mercury would have to be heated to give a pressure of 10 atmospheres, the procedure would be: Align 10 on  $P(3)$  with 0.80 on  $Z$  and read 1.255 on  $T(3)$ . Align 630, the  $T_B$  of mercury, on  $X$  with 1.255 on  $Z$  and read 790 on  $Y$ . Then 790 minus 273 gives the temperature as 567 deg. C.

In conclusion, it may be well to point out that the three  $P$  scales could have been made to read in any pressure units directly. The  $T$  scales can be scaled for any given boiling point liquid, thus forming a direct reading graphical chart of vapor pressures.

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